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Graphene-based carbocatalysts for carbon-carbon bond formation

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Abstract

Organic transformations are usually catalyzed by metal-based catalysts. In contrast, metal-free catalysts have attracted considerable attention from the viewpoint of sustainability and safety. Among the studies in metal-free catalysis, graphene-based materials have been introduced in the reactions that are usually catalyzed by transition metals catalysts. This review covers the literature (up to the beginning of April 2020) on the use of graphene and its derivatives as a carbocatalysts for C−C bond-forming reactions, which is one of the fundamental reactions in organic syntheses. Besides, mechanistic studies are included for the rational understanding of the catalysis. Graphene has significant potential in the field of metal-free catalysis because of the fine-tunable potential of the structure, high stability and durability, and no metal contamination, making it a next-generation candidate material in catalysis.

1. Introduction

Since the concept of catalysis was proposed in the 1800s,[1] most chemical reactions have been driven by metal-based catalysts. Two hundred years later, catalytic science is now in an age of transition. For example, in the early 2000s, organocatalysts, such as prolines and N-heterocyclic carbenes, were developed and attracted much attention by organic chemists.[2] Carbon catalysts, termed as carbocatalysts, can be considered as a heterogeneous version of organocatalysts. Carbocatalysts are attractive because they are a wealth of resources and can be environmentally friendly. Initially, they were applied for the functional group transformation, such as oxidation and esterification reactions.[3,4] Recently, they have been applied for the construction of C–C bonds, which are fundamental reactions in the synthesis of fine chemicals,[5] medicinal and pharmaceutical agents,[6] agrochemicals,[7] and many others;[8,9] however, almost all of them are metal-catalyzed fashions.[10–14]

1.1. Issues for metal-catalyzed systems

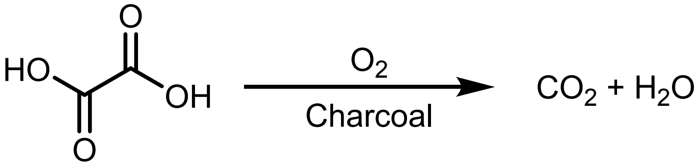
Most of the catalysis is currently ruled by the use of transition metals (TMs), either as coordination complexes, free ions, clusters, or nanoparticles, that act as active sites.[15–20] TM catalyzed C–C bond formation was evolved in the early 20th century as a leading topic in organometallic chemistry and has been one of the most direct and effective strategies in organic synthesis.[21] Now TM catalyzed C−C bond formation is regarded as the most reliable and indispensable tool.[22–24]

However, the TM catalyzed C−C bond formation reactions still have limitations due to the inherent drawbacks of the systems. Firstly, TM catalysts are generally expensive because of the high cost of TMs, support materials, and ligands. Secondly, TM is toxic and difficult to remove the trace amounts of residues from the products, which is problematic in the field of pharmaceuticals and electronic devices.[25–27] Thirdly, some of the TM catalysts are very sensitive to moisture and oxygen; thus, special environment and techniques are needed. Fourthly, sometimes cocatalysts/additives are required to initiate the reactions and enhance the selectivity of the products.[28–34] Finally, the massive utilization of TM on the industrial scale does not meet the terms of sustainable developments.[35,36] Therefore, alternative pathways to construct C−C bonds under TM free conditions are quite attractive.[37]

1.2. Metal-free catalysis: organocatalysis and carbocatalysis

Most of the organocatalysts are composed of small molecules; thus, they are used in the homogeneous systems. Organocatalysts are more straightforward, more accessible, and often less toxic compared with enzymes and inorganic catalysts. Organocatalysts can be considered as minimal biocatalysts because they are often closely approximate to the amino acid residues and co-factors that make up an enzyme. Due to the molecular character of organocatalysts, stability and recyclability are issues to be solved. For the sake of sustainability, switching the homogenous catalytic system into a heterogeneous catalytic system is desirable; thus, carbocatalyst is the green option for catalytic transformations.

Carbocatalyst can be defined as the catalyst that uses carbon materials as a catalyst for organic reactions. It should be noted that carbocatalysis has been known for decades since the first discovery of catalytic activities of carbon materials.[38] In 1925, Rideal utilized charcoal as a catalyst for the oxidation reaction of oxalic acid.[39] No conversion was observed in the absence of carbon materials.[40] The reaction is assumed to start from the aerobic oxidization of carbon to form surface-bound geminal diols. Upon further reaction with ambient oxygen, the diols devise peroxide intermediates, which then reacts with the substrate to provide carbon dioxide and water (**Scheme 1**). Charcoal also exhibits other types of oxidation and dehydration ability.[41]



Scheme 1: Charcoal-catalyzed aerobic oxidation of oxalic acid

In the 1980s, carbon was found catalytically active for the oxidative dehydrogenation (ODH) reaction of ethylbenzene to styrene.[42] Ritter used graphite for the oxidative cleavage of 4-chlorophenol, which yielded CO_2, H_2O, and HCl.[43] The reactivity of the graphite catalyst is similar to that of Fenton's reagent.[44] Howbeit, carbocatalysis did not attract enough attention at that time. Carbon-based materials can catalyze a wide range of reactions, but most of them show lower activity than metal-based catalysts. To solve the problem, chemists focused on high surface area materials. Bielawski, in 2010, reported that graphene oxide (GO) is an efficient catalyst for the aerobic oxidation of benzylic hydrocarbons.[45] After 2010, graphene-based materials have been progressively utilized as a carbocatalyst for various organic transformations such as oxidation,[46–48] reduction reaction,[49–51] and many others.[52–54]

1.3. Scope of this review

We classified the typical graphene-based materials as carbocatalyst for C−C bond forming reactions (up to April 2020) and summarized their recent advances from different aspects. The purpose of this review is to show the advantages and possibilities that carbocatalysts offer to catalysis due to their enhanced morphology and the possibility of introducing functional groups and active sites to the surface of graphene-based materials.[55] Only C−C bonds forming reactions catalyzed by graphene-based materials and active sites for these reactions will be covered here since several reviews focusing on the oxidation and reduction have already been published.[37,56–60]

Thus, after the general introduction presenting methodologies catalytic properties of carbon-based materials, which promoting the C−C reactions via a different pathway. The main body of this review deals with the reports which are expressing the catalytic activity of carbocatalysts according to the nature of the active catalytic center, such as various acid and base, radicals, and photochemical properties. The last part summarizes the mechanistic study, and the current state of the art also provides our view on future developments in this field, even some perspective to remove the misconceptions in this nascent field.

2. Preparation methods of graphene-based carbocatalysts

Preparation of graphene and its derivatives have already been reported.[61–67] Therefore, this chapter only focuses on the preparation methods of graphene materials suitable for catalyst applications. GO and reduced graphene oxide (rGO), which contain a certain degree of defect sits, are by far the most common graphene-based carbocatalysts. GO is produced by Brodie,[68] Staudenmaier,[69] Hoffman,[70] and Hummer's method[71] with the aid of strong acid (nitric and/or sulfuric acid) and oxidant (chlorate or permanganate); however, the real structure of GO is still under argument (**Figure 1**).

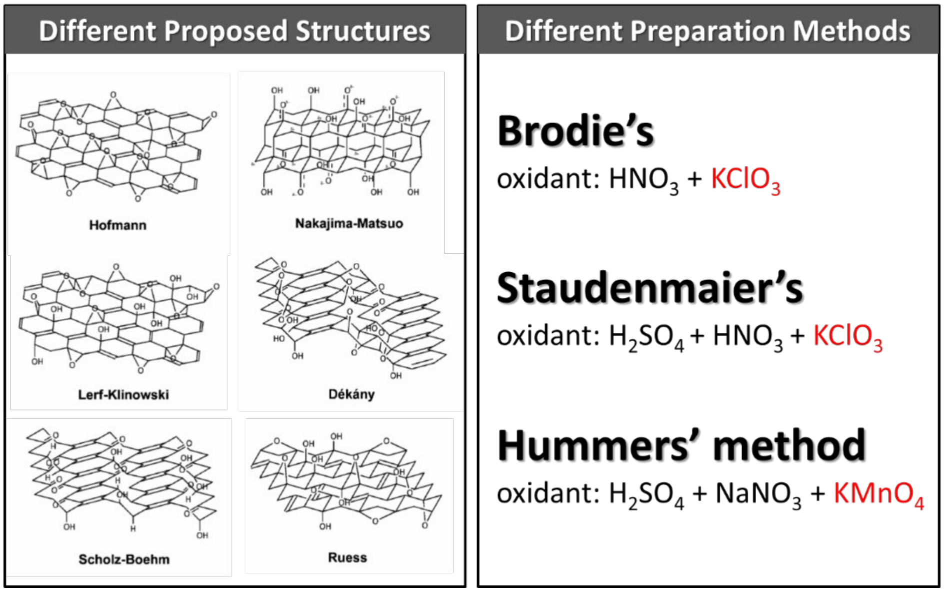


Figure 1: Proposed structures of GO and methods for the synthesis of GO.

The most popular method is Hummer's method, which has been further improved and modified.[72] For example, $NaNO_3$ converts to various harmful and environmentally unfriendly gases; thus, analogous methods that do not utilize this salt are desired. For instance, Kovtyukhova demonstrated that the pre-treatment of graphite with P_2O_5 and $K_2S_2O_8$ in H_2SO_4 enabled the $NaNO_3$-free synthesis of GO.[73] Likewise, pre-treating graphite with MnO_2[74] or irradiation of microwave[75] also promotes the efficient formation of GO (**Figure 2, step 1)**. Tour utilized H_3PO_4 instead of $NaNO_3$,[76] and Shi noted that water enhances the oxidation of graphite (**Figure 2, step 2**).[77] Besides, treatment methods after oxidation were also investigated, and water and H_2O_2 are reported to accelerate the oxidation degree of GO.[78,79] Despite many improved methods for GO production, as mentioned above, we have clarified that the pre-oxidation of graphite is not necessary and that the critical reagents needed to facilitate Hummer's-type oxidations are $KMnO_4$ and concentrated H_2SO_4. Also, the use of less than 5 vol.% of water was found to facilitate the formation of single-layer GO.[80]

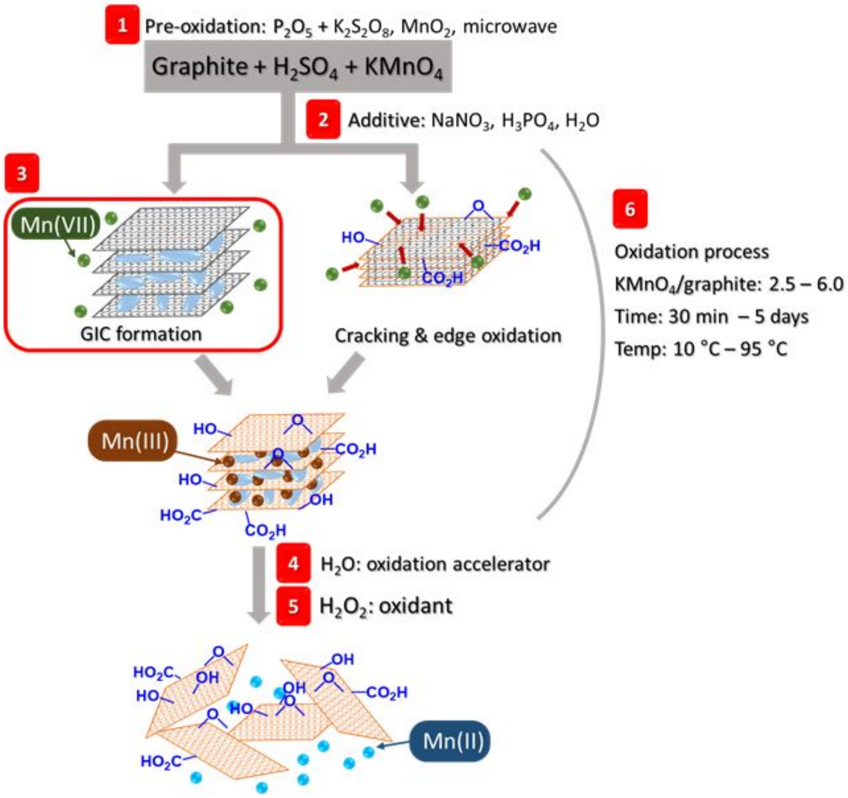


Figure 2: Summary of various synthesis methods of GO from graphite and remarks.

Due to the high quantity of the oxygen functional groups on GO and the reactivity of the oxygenated functional groups, GO can inevitably undergo decomposition and aging under catalytic conditions. To tailor the properties of GO on purpose, enormous research has been done to remove the oxygenated functional groups from GO (**Table 1**).[81,82] Various methods and techniques, such as chemical agents,[83] electrochemistry,[84,85] UV irradiations,[86,87] microwave irradiations,[88] micro-organisms,[89] ion bombardment,[90] or thermal treatments,[84,86,91] were developed to tune the properties of rGO. The material design includes the C/O ratio, selective removal of the oxygenated groups such as hydroxyl, carboxyl, and epoxy, healing of the surface defects to maintain and improve the desired chemical and physical properties required for carbocatalyst.[98,99] Further discussion and comments about the preparation procedure of carbocatalyst will be shown in each section.

Table 1: Summary of various reduction methods of GO to rGO.

Method	**Characteristics**
Chemical agent	The reduction is performed in liquid. Commonly used chemical agents are as follows. Borohydride: mainly reducing carbonyl groups. Aluminum hydride: removing carboxylic acid and ester. Hydrohalic acid: removing hydroxy and epoxide.
Electrochemical reduction	The reduction of GO occurs at the cathode, avoiding the use and contamination of chemical agents.
UV irradiation	Elimination of hydroxy and carbonyl functional groups occurs.
Microwave irradiation	Solid-state microwave irradiation not only removes oxygen-containing groups but also repair defects of the graphene sheets. Microwave removes C=O efficiently.
Micro-organism	Elimination of epoxy and alkoxy functionalities occurs.
Ion bombardment	Epoxy and carbonyl could be retained mainly.
Thermal treatment	High-temperature treatment results in much higher degree reduction as compared to chemical reduction.

3. Acid/base catalysis by graphene-based catalyst for the construction of C−C bonds

Acid-base catalysis is a fundamental discipline in organic chemistry, providing a novel contribution to the development of green chemical processes.[94] Homogeneous acid/base catalysts are widely employed for various chemical transformation in chemical industries and fine chemicals.[95,96] The traditional homogeneous catalysts are highly efficient but difficult to recycle. In contrast, solid catalysts have long been developed, which is easily separated from the products.[97] Solid acid catalysts are mainly based on metallic species such as silica-alumina,[98] mesoporous materials,[99,100] and zeolites.[101] Carbon materials bearing acid moieties[102,103] and metal-organic frame works[19,104,105] have also been developed.[106] As for base catalysts, zeolites, modified zeolites, alkaline earth oxides, alkali metals on supports, KNH_2 on alumina, KF on alumina, hydrotalcite, and oxynitrides are developed.[107–109] A problem with traditional solid acid or base catalysts are their lifetime, due to the strong chemisorption of water molecules on the active sites of the catalysts. Accordingly, water-tolerant solid acid catalysts with high performance are required.[110] Graphene-based materials are expected to solve the problem because of their hydrophobicity, stability, and tunable properties.

3.1. Brønsted acid/base reactions by graphene-based catalyst

3.1.1. Strategy and concept

The acidic/basic properties of graphene-based materials rely on the surface functional groups. The acidity of carbon materials is generally weak and can be enhanced by introducing sulfonated functional groups,[111–113] which are much more acidic than carboxylic acids. While the sulfonated carbocatalysts suffer from the leaching of -SO_3H moieties at high temperature.[114]

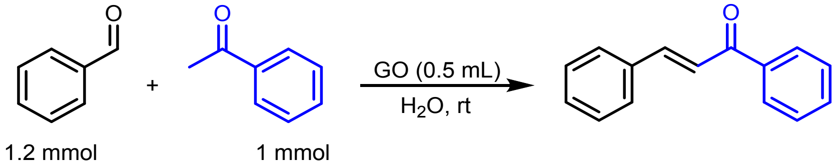
Contrarily, carbon and oxygen groups are not basic. The basicity can be enhanced by doping nitrogen (N) into or grafting amine groups onto the carbon frameworks. Recent theoretical calculations show that the pyridinic N group is more basic than other N-containing functional groups.[115] However, the pyrone-type structure, where nitrogen is located near a carbonyl group, exhibits even stronger basicity than pyridine-type nitrogen atom.[116]

In this section, we will summarize the graphene-based Brønsted acid/base catalysis for the construction of C−C bonds, which is mainly based on the aldol-type reactions.

3.1.2. Aldol-type reaction

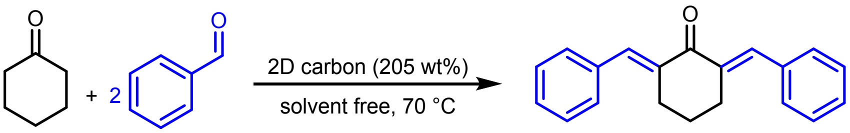
The aldol reaction is one of the essential methods of forming carbon-carbon bonds. The products, chalcone derivatives, are precursors for the biosynthesis of flavonoids and isoflavonoids.[117] The efficiency of GO as a catalyst was first tested in aldol reaction over various electron-withdrawing and electron-donating aromatic aldehydes with acetophenone under solvent-free conditions (**Scheme 2**).[118] In this study, the authors mentioned GO works as a base catalyst. In contrast, Zali modified the surface of carbon materials with $-SO_3H$, which showed higher catalytic activity than sulfuric acid.[119] Asphaltene oxide (AO) produced by the Hummers' type oxidation of asphaltene also catalyze aldol reaction.[120] The origin of catalytic activity was examined by changing various parameters such as the effect of elemental composition, the dosage of catalyst, and particle size. In the presence of a base (i.e., pyridine), the product was not observed due to a neutralization reaction. Thus, the catalytically active sites are acidic sites on the carbocatalyst. GO catalyzed reactions are sometimes argued because of the contamination of metal species, removal of its oxygenated groups, and residual acids/oxidants.[121]

Cid developed a bifunctional amine catalyst, in which piperazine was grafted on to rGO.[122] The presence of two nitrogen atoms in piperazine provides bifunctional catalysis: iminium formation and basic sites. Non-functionalized rGO was inactive for aldol reaction.



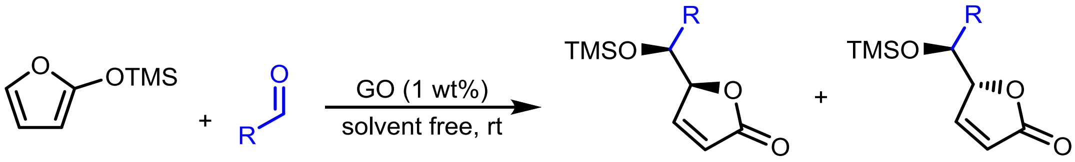
Scheme 2: Aldol condensation between acetophenone and benzaldehyde catalyzed by GO.

Lin utilized a nanocage carbon-bearing benzene sulfonic acid catalyst and evaluated its catalytic activity for cross aldol condensation of ketones and aromatic aldehydes (**Scheme 3**).[113] The yield of the product by recycling of the catalyst is gradually decreased; it may be attributed to the loss of catalyst during recycling and the loss of active sites.



Scheme 3: 2D carbon as an acid catalyst for the cross aldol reaction.

Acocella reported GO and exfoliated-GO (e-GO) as efficient catalysts for aldol coupling of 2-(trimethylsilyloxy)furan with an aldehyde (**Scheme 4**).[123] In contrast to the conventional catalysts, the anti-diastereoisomer was obtained with high diastereoselectivity (dr up to 85:15). GO, and e-GO showed comparable activity and diastereoselectivity (85–90% yield, dr=75: 25–77: 23). A practical advantage of this method involves the solvent-free conditions. The authors proposed that the catalytic activity of GO was associated with surface carboxylic acid (−COOH) and hydroxy (-OH) functional groups. Activation of aromatic aldehydes occurs by π-stacking interactions with the carbocatalyst; in contrast, the aliphatic substrates were found less active.

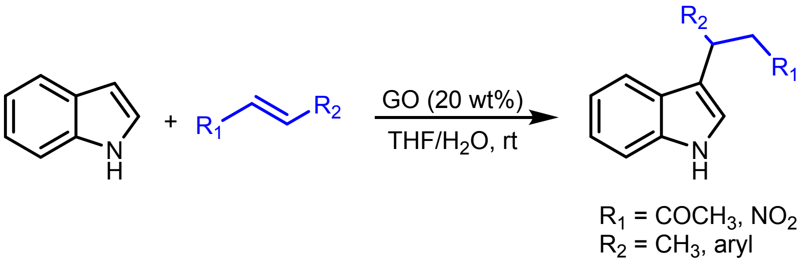


Scheme 4: GO catalyzed Mukaiyama aldol reaction.

Jia synthesized graphene acid (GA), using graphite flake, $K_2Cr_2O_7$, H_2SO_4, and CH_3CO_3H as a raw material.[102] GA was utilized as a catalyst for the aldol type (Claisen-Schmidt reaction) (**Scheme 2**). Xu used sulfonic acid-modified carbon as a catalyst for the condensation reaction of acetophenone with benzaldehyde under a solvent-free condition.[124] The catalyst was reused up to three cycles and did not lose activity and selectivity. The weight of catalyst increased slightly, and no sulfate ion was detected in the reaction mixture. Nevertheless, the acid capacity of the catalyst was found to decrease from 1.40 mmol g^{-1} to 1.05 mmol g^{-1}, exhibiting that reactants or products might be deposited on catalysts and deactivate the active sites.

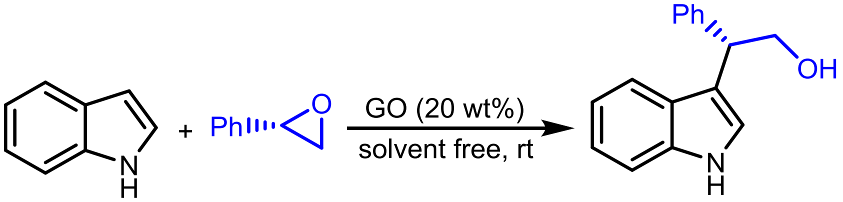
3.1.3 Freidel-Crafts-type reaction

The alkylation of arenes is generally performed with TM catalysts to produces pharmaceutical ingredients and fine chemicals. Interestingly, graphene-based materials can also catalyze the direct Friedel-Crafts alkylation of arenes with styrene and alcohols.[125] The electrons on graphene are considered to influence the electrophilic intermediate. Kumar and Rao used GO as a catalyst in the Friedel-Crafts-type addition reaction of indoles to α,β-unsaturated ketones, or nitrostyrene (**Scheme 5**).[127]



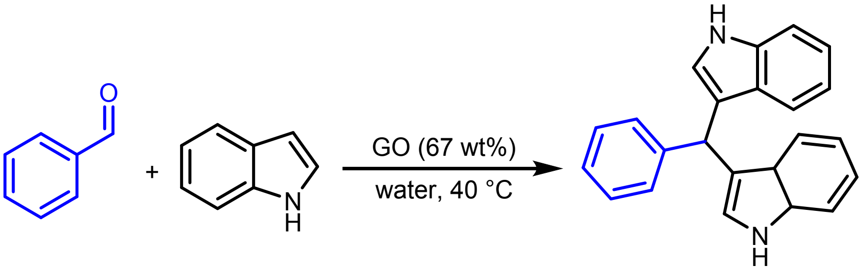
Scheme 5: Friedel-Crafts addition of indoles to α,β-unsaturated substrate catalyzed by GO.

Guerra reported GO as a catalyst for the Friedel-Crafts reaction between indole and epoxides (**Scheme 6**).[128] graphite and carbon were used as catalysts for comparison, but showed negligible yield, suggesting the activity of GO is probably due to the carboxylic and hydroxy groups. The product was obtained regioselectively with complete inversion, indicating that the GO-catalyzed reaction was S_N2 fashion. This reaction is typically catalyzed by nanocrystalline TiO_2,[129] Fe_3O_4, or $CuFe_2O_4$.[130]



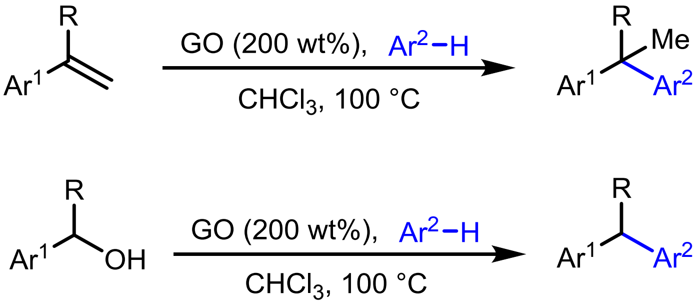
Scheme 6: Regioselective ring-opening reaction of styrene oxide with indole catalyzed by GO.

Wang utilized GO as a solid acid catalyst for the synthesis of bis(indolyl)methanes from aldehyde and indole (**Scheme 7**).[131] GO was recycled ten times without any loss of activity. It was proposed that the carboxy group on GO played an essential role in the reaction.



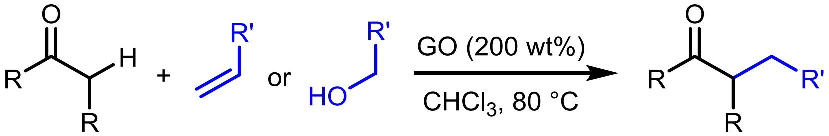
Scheme 7: GO as a solid acid catalyst for the synthesis of bis(indolyl)methanes from aldehyde and indole.

Hu utilized GO for Friedel-Crafts alkylation reaction of styrene or alcohol with arenes (**Scheme 8**).[132] Activation of both coupling partners occurs due to the polar and aromatic functional groups on the surface of GO is a key step to the successful transformation. However, 200 wt% of GO is necessary.



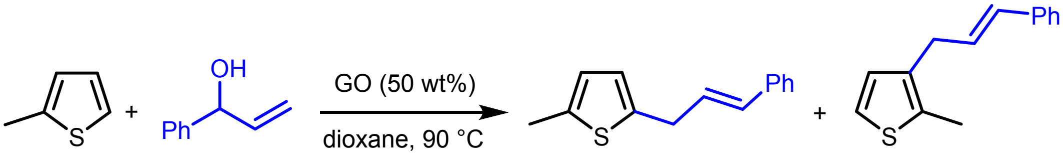
Scheme 8: GO-catalyzed direct alkylation of arenes.

Inspired by the interest in carbon-based materials[132,133] and realizing the importance of direct carbonyl α-alkylation methods, they further reported the general strategy for ketone-alkylation using olefins and alcohols as alkylating agents catalyzed by 200 wt% of GO (**Scheme 9**).[134] The activation of the coupling partners occurs on the surface of GO via hydrogen bonding. GO may be deactivated by the loss of the oxygenated functional groups, but a negligible decrease of oxygen was observed after the reaction, keeping its high activity for several reuses.



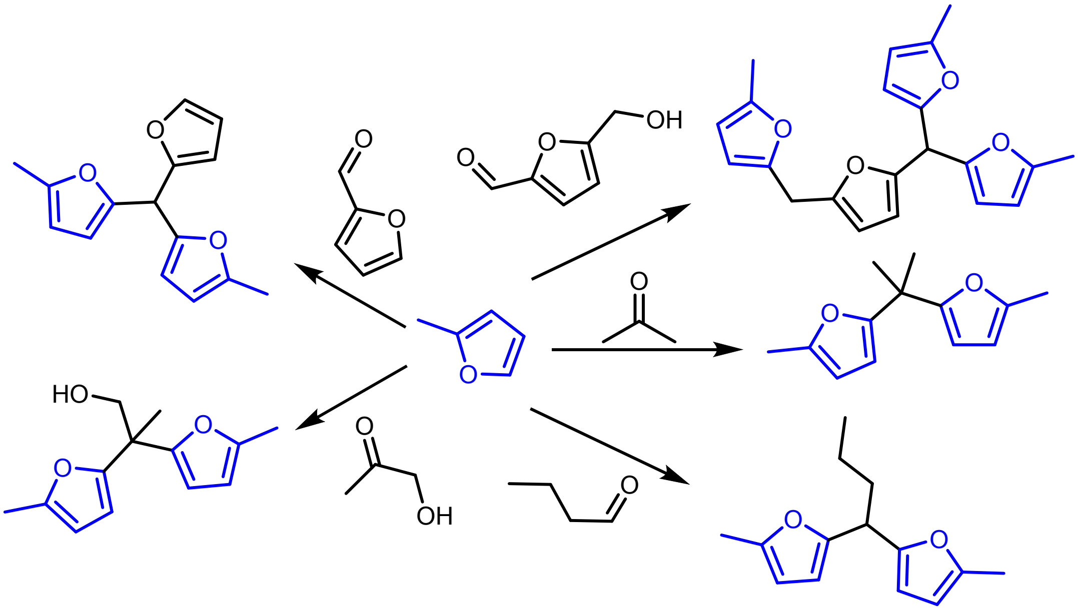
Scheme 9: GO catalyzed alkylation of ketones with olefine/alcohol.

A large amount of GO loading is necessary in some cases; therefore, it is unclear whether GO is an actual catalyst or stoichiometric reagent. Combining the DFT calculation and employing model compounds with specific oxygenated functional groups, Favaretto demonstrated GO acts as a catalyst in the Friedel-Crafts type reaction between thiophenes and allylic alcohols (**Scheme 10**).[135] It was elucidated that the active sites of GO were the Brønsted acidic sites.



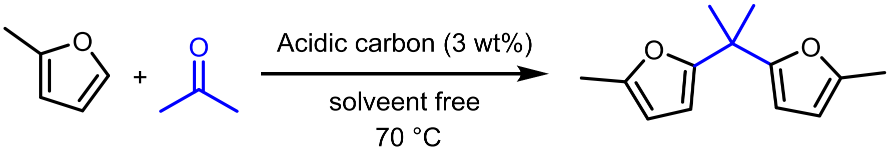
Scheme 10: GO catalyzed alkylation of thiophene with allylic alcohol.

Dutta used GO with higher oxygen content than the conventional GO, and applied for C−C bond forming reaction using a biomass-derived furan derivative (**Scheme 11**).[136] The highly oxidized GO showed higher activity over conventionally used zeolites and commercial GO. The catalyst became inactive after the fourth cycle due to the loss of its surface oxygen functionalities and defects.



Scheme 11: Highly oxidized GO as carbocatalyst for the alkylation, reaction conditions; GO (3 wt%), at 80 °C for 6 h, under neat condition.

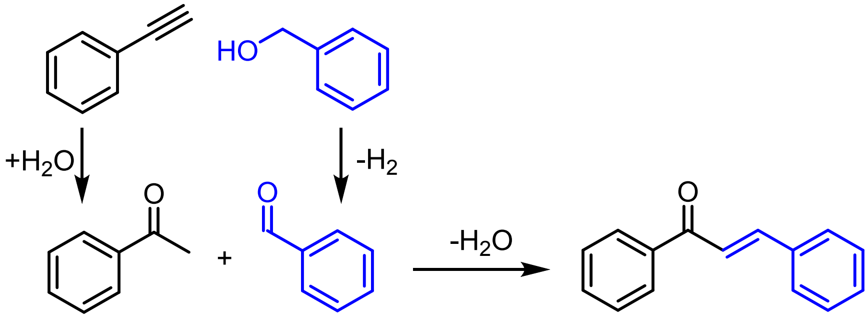
Kanwar reported Na-lignosulfonates (LS) derived mesoporous solid acid catalyst for the C−C coupling of furan with carbonyl compound (**Scheme 12**).[137] The observed catalytic activity and stability of the LS derived acidic carbocatalysts were attributed to the $-SO_3H$ groups covalently incorporated into their structural carbon framework and the promotional effects of hydrophilic surface functional groups (−COOH, and −OH) favoring adsorption of oxygenated reactant molecules.



Scheme 12: Acidic carbon-catalyzed coupling reaction of furan and carbonyl compound.

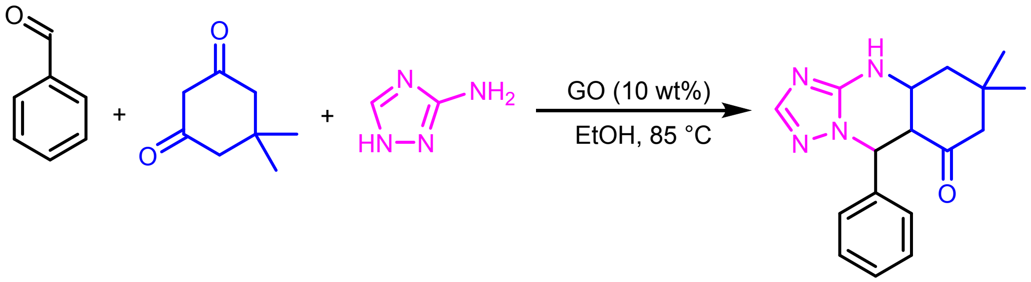
3.1.4. Multistep reactions

GO was also found to act as a tandem hydration-oxidation aldol coupling catalyst in facilitating the formation of chalcones in one-pot with alkynes and alcohols as the starting materials (**Scheme 13**).[138]



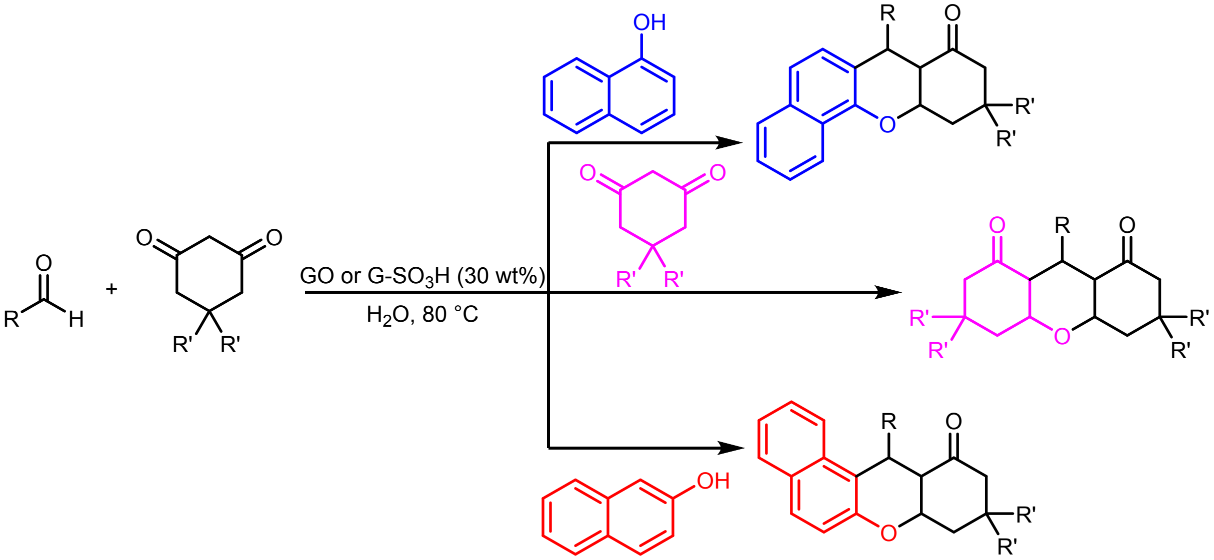
Scheme 13: GO catalyzed hydration and oxidation followed by aldol reaction; starting materials 0.5 mmol each, GO 200 mg, 80 °C, 14 h, under solvent-free conditions.

The inherent Brønsted acidity of GO derived from oxygenated groups on edge has been well exploited in various organic synthesis.[132,139,140] In this context, Chen proposed an approach that a carbocatalyst as a Brønsted and Lewis sites can catalyze a multicomponent synthesis of triazoloquinazolinone compounds.[141] GO having the highest degree of oxidation, also having the highest amounts of acidic sites, allowed 95% yield. The results from the FT-IR spectroscopy, temperature-programmed decomposition mass spectrometry, and X-ray photoelectron spectroscopy identified that epoxide (Lewis sites) and carboxy groups (Brønsted) are responsible for the enhanced carbocatalytic activities involving Knoevenagel condensation (**Scheme 14**).



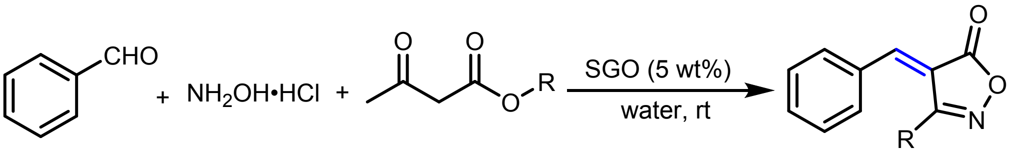
Scheme 14: GO catalyzed multicomponent reaction.

Shbaani reported the synthesis of xanthenes and benzoxanthenes using sulfonated GO as a catalyst for the successive aldol-cyclization reactions (**Scheme 15**).[142]



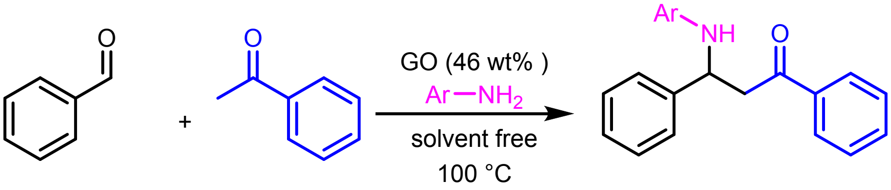
Scheme 15: Synthesis of xanthene and benzoxanthene derivatives using sulfonated GO.

Pranab demonstrated the sulfonated GO (SGO) as a solid catalyst for the pharmaceutically promising substituted isoxazole derivatives in the presence of water as a solvent (**Scheme 16**).[143] After the 5th cycle, the catalytic activity was decreased due to the loss of the sulfur from 3.12 to 0.68 wt%.



Scheme 16: Sulfonated GO-catalyzed synthesis of substituted isoxazoles.

Khalili reported that GO worked as an efficient catalyst for one-pot sequential aldol coupling/aza-Michael addition in a single reaction vessel (**Scheme 17**).[144] The addition of 30 mol% of tetrabutylammonium bromide improved the product yield. Rashinkar achieved three component synthesis of quinolines using aldehyde, amine, and alkyne.[145]



Scheme 17: GO-catalyzed sequential aldol coupling/aza-Michael addition of amines to chalcones.

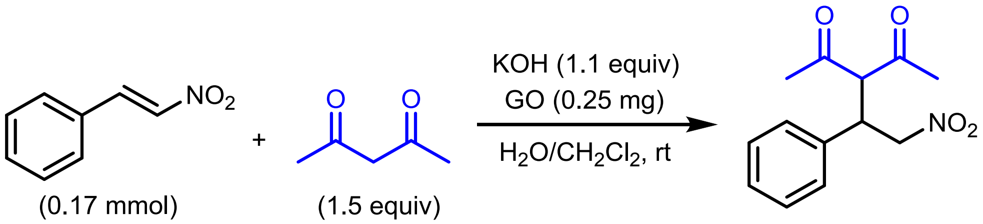
3.2. Lewis Acid/Base catalysis utilizing carbocatalysts

3.2.1. Strategy and concepts

Lewis acid/base is widely used in organic synthesis. It is quite challenging to devise an active Lewis acid/base catalyst for the construction of C−C bonds. Because of the inherent carboxy groups, GO commonly acts as a solid acid in various C−C bond-forming reactions, as shown in the previous section. However, due to the presence of hydroxy, epoxy, and carbonyl groups, GO can serve as a Lewis base. Withal, to explain the activity of GO for activation of substates, an analogy with organocatalysis was suggested. It has been well documented in the literature that there are discrete organic molecules are comprising Lewis acid-base pairs rigidly separated at a short distance without undergoing neutralization (frustrated Lewis acid-base pairs).[146]

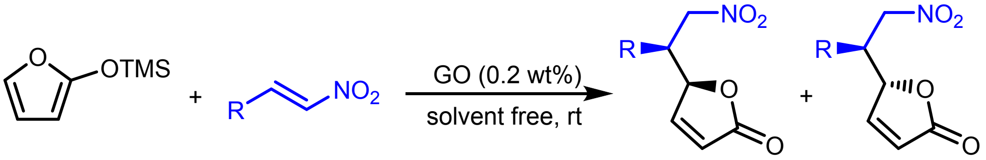
3.2.2. Michael addition

The creation of new C−C bonds via Michael addition is an essential transformation in organic chemistry.[147,148] Lee used GO as a recyclable phase transfer catalyst to the coupling of acetylacetone and trans-β-nitrostyrene (**Scheme 18**).[149] GO can be dispersed on CH_2Cl_2 and H_2O because they possess hydrophilic oxygen functional groups and hydrophobic carbon frameworks. The oxygen functional groups can carry potassium ion from the aqueous phase to the organic phase. Based on the experimental data, the oxygen functional groups in GO, including carbonyl, carboxylic, lactone, quinone, and especially epoxy and hydroxy groups, are responsible for the catalytic activity. The abundant oxygen functional groups of GO act as cation holders which make hydroxide anions stronger in the organic phase. GO showed superior catalytic activity than well-known crown ether phase transfer catalyst. Ma modified GO with diethylenetriamine (GO-DETA), which has primary and secondary amino and carboxy groups.[150] The GO-DETA was applicable for Michael addition in water. Baharfar covalentry functionalized GO with an organic superbase, and applied for Michael reaction.[151]



Scheme 18: Micheal addition catalyzed by GO as a phase transfer catalyst.

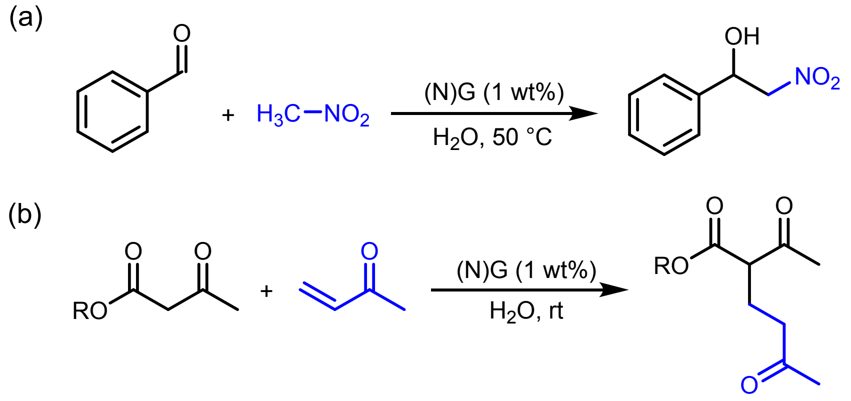
Acocella reported GO worked as catalysts for Mukaiyama-Michael coupling of 2-(trimethylsiloxy)furan with β-nitroalkenes (**Scheme 19**).[152] This system, in contrast to traditional catalysts, the anti-diastereoisomer is obtained with high diastereoselectivity (up to 85:15). rGO, carbon black, and large-surface-area graphite also exhibited catalytic activity in the same reaction, albeit resulted in lower yields of the product (65-70%), while maintaining high anti-diastereoselectivity. The high anti-selectivity of the process was proposed to arise from a combination of (i) π-stacking interactions between β-nitrostyrene and the π-domain of the catalyst and (ii) van der Waals interaction between the trimethylsilyl group and hydrophobic domain of the catalyst.



Scheme 19: GO-catalyzed Mukaiyama-Michael coupling of 2-(trimethylsiloxy)furan and β-nitroalkenes.

Base catalysts are used in numerous classical condensation reactions, such as Michael and Henry additions. Parvulescu utilized N-doped graphene ((N)G) as a catalyst in such reactions

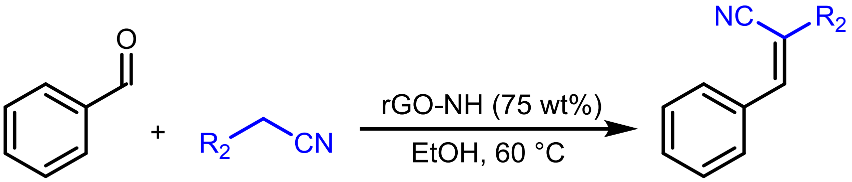
(**Scheme 20**).[153] (N)G was prepared by chitosan pyrolysis. The acid-base titrations using NH_3 and CO_2 as probe molecules indicated that (N)G has a considerably higher density of basic sites than acid sites. The DFT calculation revealed that the active sites are pyridinic nitrogens, particularly those at zig-zag edges.



Scheme 20: N-doped graphene-catalyzed (a) Henry addition, and (b) Michael addition reaction.

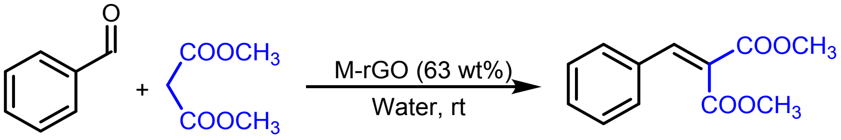
3.2.3. Knoevenagel condensation

Carbon materials exhibit weak intrinsic basicity, and they typically cannot show catalytic performance. In contrast, doping with heteroatoms or grafting can enhance the basicity of carbon materials, enabling the Knoevenagel condensations. Cid functionalized GO with piperazine to provide a bifunctional catalyst (rGO-NH) and applied to Kneovengel condensation.[122] The reaction afforded high yields with different nucleophiles and a variety of aromatic aldehydes with an electron-donating or electron-withdrawing group **(Scheme 21)**.



Scheme 21: Knoevenagel reaction catalyzed by rGO-NH

Amino-terminated poly(amidoamine) (PAMAM) dendrimers were used as both a reducing and a stabilizing agent for GO. The advantage of this approach is that the reduction time of GO is shorter than those of other reducing agents, such as hydrazine.[154] The PAMAM modified rGO (M-rGO) was employed as a catalyst for the Knoevenagel condensation between aldehyde and malonic ester (**Scheme 22**).[155] As also shown by Zhang, amine-grafted GO can be a catalyst for Knoevenagel condensation reactions.[156]

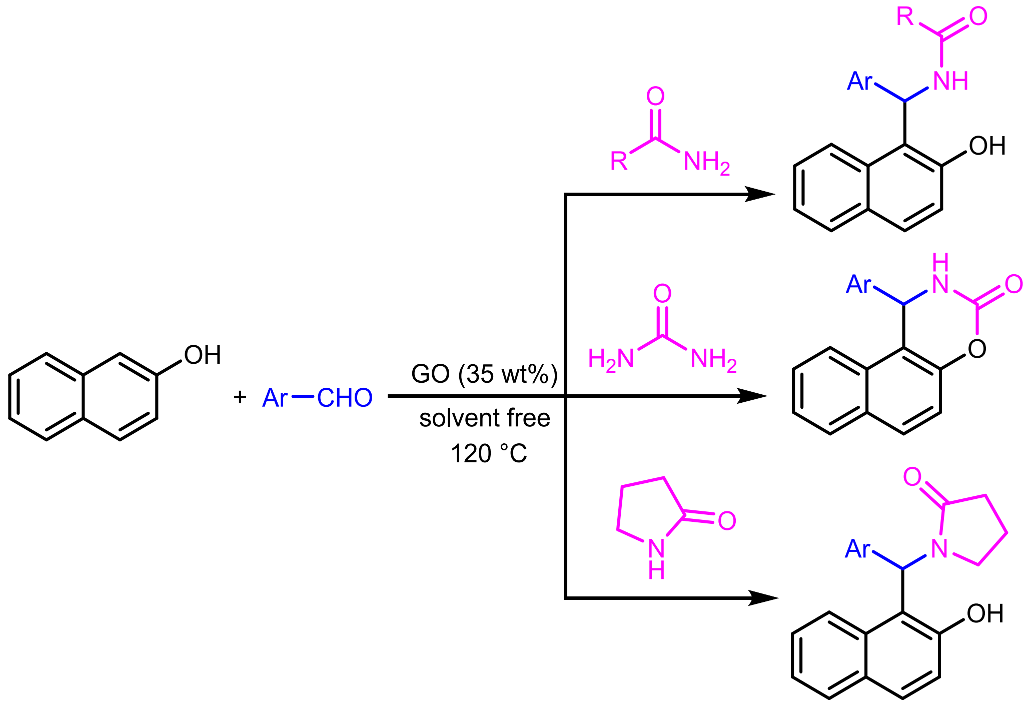


Scheme 22: Knoevenagel condensation reaction catalyzed by modified rGO.

The grafting of GO with amine has been generally performed in severe conditions, e.g., high temperature and tedious process. A more straightforward approach was developed by Li, in which the grafting of ethylenediamine on GO was achieved under a mild reaction condition through epoxy ring-opening amination.[157] The catalytic activity of the amine grafted GO was evaluated for Knoevenagel condensation reactions in mild conditions. Later on, the same group established another strategy, in which ammonia-modified GO was synthesized by the gas-solid acid-base reaction between ammonia and carboxy groups on GO at room temperature.[158] The prepared catalyst was utilized for Knoevenagel condensation reactions and found recyclable.[157]

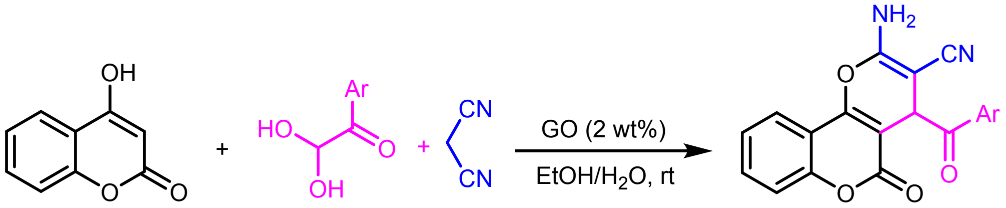
3.2.4. Miscellaneous reaction

Kapoor reported GO-catalyzed solvent-free functionalization of naphthol with aldehydes and amides (**Scheme 23**).[159] These GO-catalyzed reactions present several advantages, such as high product yield, short reaction time, ease of workup, and environmentally safe processes.



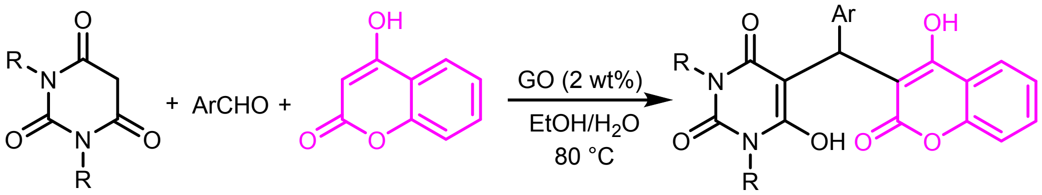
Scheme 23: Three-component reaction using GO as a catalyst.

Karami demonstrated that the one-pot and three-component coupling among 4-hydroxycoumarin, aryl glyoxals, and malononitrile were efficiently catalyzed by GO to produce pyranocoumarins (**Scheme 24**).[160]



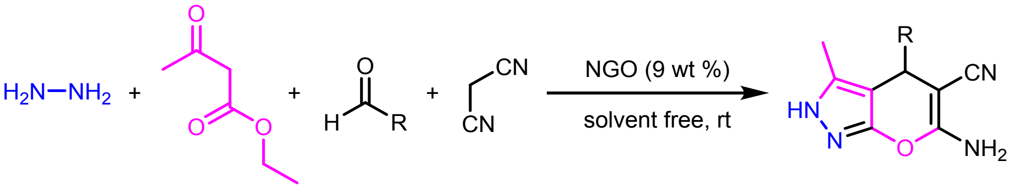
Scheme 24: Multicomponent condensation reaction catalyzed by GO as a catalyst.

Karami described the three-component coupling among barbituric acids, 4-hydroxycoumarin, and a wide range of aryl aldehydes to obtain novel barbituric acid derivatives (**Scheme 25**).[161] Brønsted acidic and Lewis base on the GO work as catalytically active sites for this reaction.



Scheme 25: GO-catalyzed three-component condensation of barbituric acids.

Suresh reported a simple solid-base nitrogen-doped GO (NGO) as a heterogeneous catalyst for the tandem synthesis of pyranopyrazoles under neat conditions (**Scheme 26**).[162] The presence of high density of various nitrogen sites, specially graphitic nitrogen are acting as potential catalytic active sites that remarkably catalyze the reaction. The results of reusability studies demonstrated that the NGO remains equally active and exhibit high stability even after eight consecutive catalytic runs.



Scheme 26: NGO catalyzed synthesis of pyranopyrazole.

4. Radical properties of the carbocatalysts

4.1. Strategy and concept

Free radicals play a crucial role in many fields such as catalysis, chemical synthesis, materials science, and biomedical.[163–165] To date, generating stable free radicals remains a challenge, due to the coupling of individual radicals. It has been revealed that, compared with CNTs and nanodiamonds, graphite/graphene-based materials are a carrier of free radicals due to its large number of an unpaired electron, edges, and internal structural defects.[166–169] It means that compared with graphene, GO shall have a larger content of free radicals. The π-conjugated planar structure of graphene makes it physically difficult for the radicals to react with each other, which means graphene may be able to serve as a carrier of stable free radicals. Recent efforts have focused on theoretical prediction and computational modeling of graphene radicals.[170–172] Furthermore, GO can be reduced by different methods, such as light irradiation, thermal, and chemical treatments.[173] These treatments can remove the different functional groups on GO, producing dangling bonds on its surface,[82,174–176] which may create more radicals.[177] It is found that the free electron can be localized at the edge or defect site of GO (**Figure 3**)[178], which makes them more reactive and act as stable free radicals. In this section, we will review the role of radical on GO for the C−C bond formation reactions.

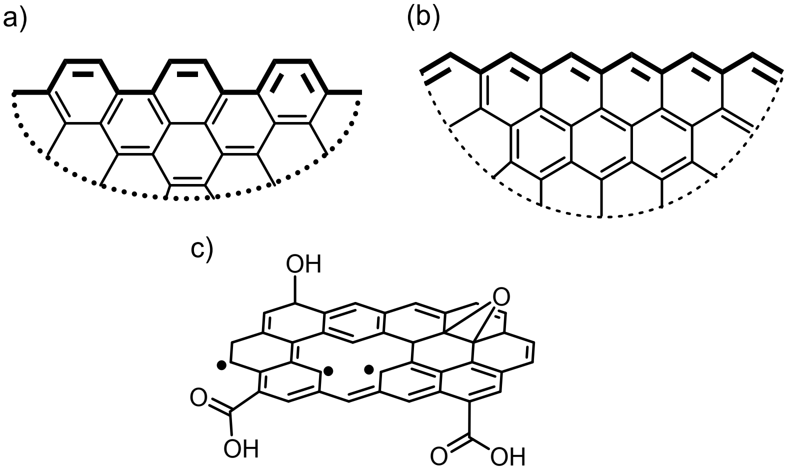
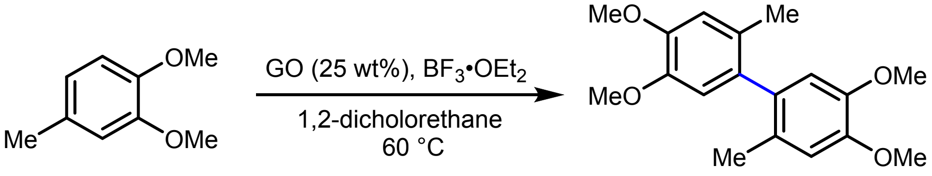


Figure 3: The chemical nature of free edge sits in sp^2 hybridized carbon a) armchair sites and b) zig-zag sites, c) schematic representation of radicals on GO.

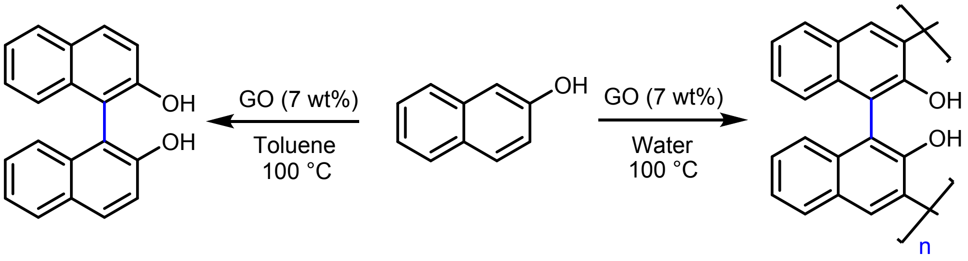
4.2. CH-CH homocoupling reaction catalyzed by carbocatalyst

The activation of C−H bonds by carbocatalysts to form C−C bonds has recently emerged as a hot topic in carbocatalysis. The development of metal-free carbocatalysts for CH−CH type coupling, one of the most difficult chemical transformations, has rarely been reported.[56] We reported the use of GO as a catalyst for the formation of the C−C bond of anisoles and derivatives, of which mechanism was clarified as a free radical pathway.[179] The reaction conditions were initially optimized in the oxidative coupling of 3,4-dimethoxytoluene to the corresponding dimer. It was found that GO in conjunction with $BF_3{\cdot}OEt_2$ afforded the biaryl product in excellent yield; however, GO was reduced and lost its activity after the reaction (**Scheme 27**). It was demonstrated that the developed conditions are superior to those using hypervalent iodine reagent, $PhI(OAc)_2$. Impressively, the substrate scope was shown to include halogen-containing substrates, which could be used as handles for traditional cross-coupling reactions. The reaction mechanism was investigated by adding a radical scavenger (TEMPO) and monitered the reaction by electron spin resonance (ESR), confirming the presence of radical species in situ.



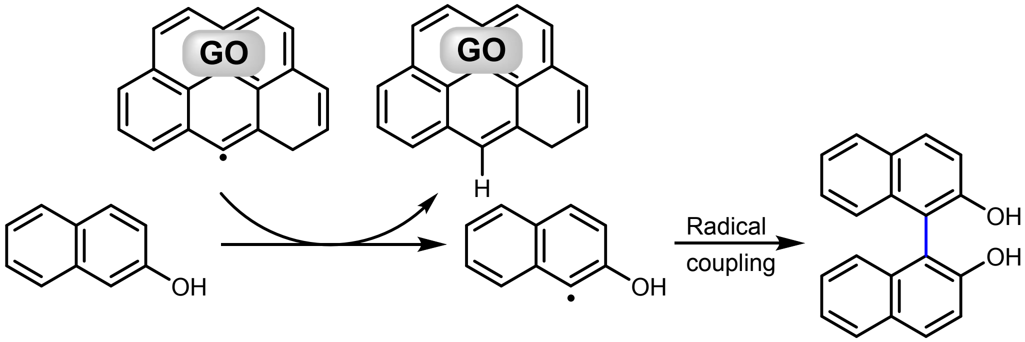
Scheme 27: GO-promoted homocoupling of anisole derivatives.

The oxidative homo-coupling reaction of β-naphthols provides binaphthols, which are widely utilized as ligands and DNA cross-linking reagents.[180,181] Commonly, binaphthols are synthesized by Fe,[182] Cu,[183] and V[184] catalysts. To overcome these drawbacks, Ranganath demonstrated that GO worked as an efficient catalyst for the oxidative coupling of 2-naphthols.[185] Solvent plays an important role; the reaction in aqueous media leads to polymerization of the product, while organic solvents selectively formed binaphthol (**Scheme 28**). Furthermore, to determine the effect of GO, various carbon materials such as graphite, carbon nanotubes, functionalized CNTs, and activated charcoal were utilized as catalyst under the same reaction conditions, but lower product yields were observed. A base such as NaOH or KOH was needed to obtain the product in >90% yield; without the additive, only 20% of the product was obtained. The GO catalyst could be recycled three times, but the active site and the effect of solvents are not clear at this moment.



Scheme 28: Oxidative coupling of β-naphthol catalyzed by GO.

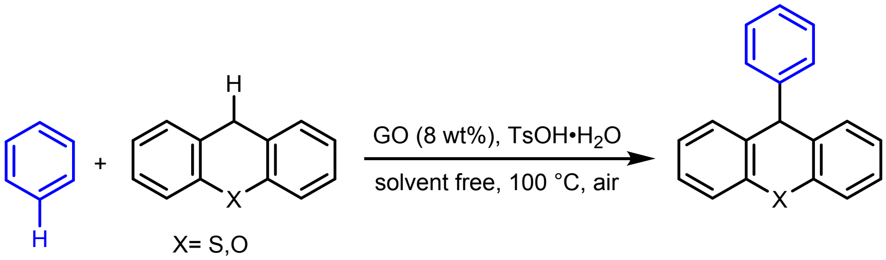
Gong explored the active catalytic center on GO using various small molecules containing different oxygen groups, such as hydroxy, carbonyl, epoxide, and carboxylic acid, and different π-conjugated systems.[186] However, no product was detected, indicating that only a single functional group does not attribute to the catalytic property of GO. Other carbon materials, such as activated carbon, graphite, acetylene black, and rGO, were also tested, but all were found inactive. This finding indicated that the catalytic activity of GO was irrelevant to the π-conjugated system. Thus, the author hypothesized that the unpaired electrons on the GO might play a crucial role in the coupling reaction, which is already proposed in the hydrogenation reaction[187] (**Scheme 29**). In this context, hydrogen can be captured by the unpaired electron on the GO edge, and the aromatic radical is generated. Finally, the radical coupling reaction subsequently occurs, and the desired product can be produced. Oxidative carbocatalysis has the potential to replace many transition metal-catalyzed or stoichiometric oxidative reactions. But, it should be commented that further experiments are needed to rule out the possibilities of metal-induced catalysis, because contamination of ppm level of metal species may not be prevented in the most of the carbon materials.[188]



Scheme 29: Mechanism of homo-coupling of β-naphthol catalyzed by GO.

4.3. CH−CH cross-coupling reaction catalyzed by carbocatalyst

CH−CH cross-coupling is one of the most challenging reactions. Recently, fine-tuning the substrates and reaction conditions enabled the selective functionalization of C−H bonds. Loh and Su carried out the cross-coupling of xanthenes or thioxanthene with arenes in the presence of GO with $TsOH{\cdot}H_2O$, yielding 85 % of the corresponding CH−CH cross-coupling products with high selectivity (**Scheme 30**).[189] The mechanistic study showed that the reactivity of GO was corresponded to the concentration of quinone type species (C=O) but had no apparent relationship with the content of epoxide and hydroxy groups. The use of small-molecule analogs allowed mimicking the active catalyst site (**Figure 4**). Molecular analogs such as benzyl alcohol, hydroxy, epoxides, and carboxy groups were not effective. Whereas their zig-zag edges counterpart such as tetracene and pentacene, afford higher reactivity (54 %). Anthraquinone, which incorporates both the zig-zag edges and the C=O species, provided the best performance (76 %) among all the tested small-molecule analogs.



Scheme 30: GO-catalyzed CH−CH cross-coupling reaction of xanthene with arenes.

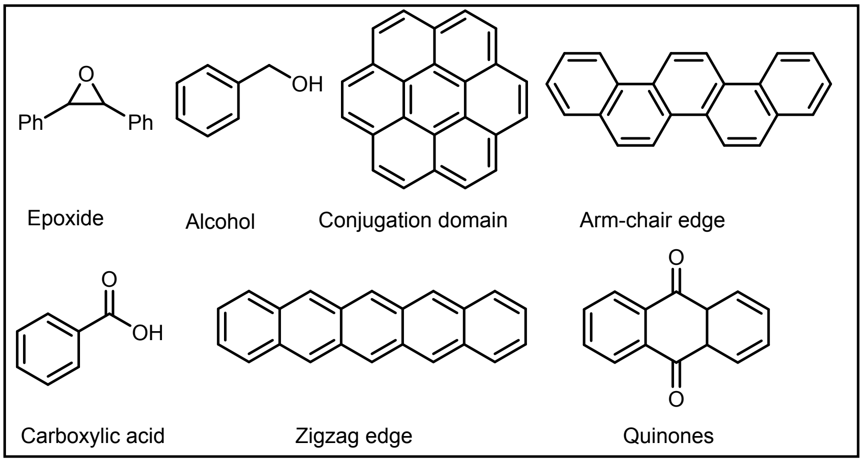
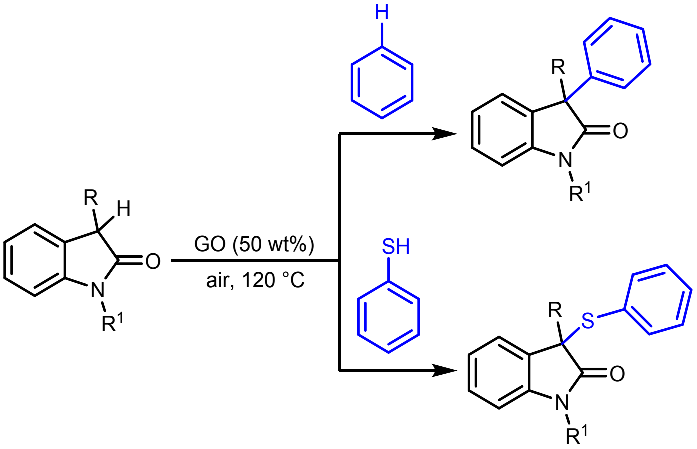


Figure 4: Different model compounds utilized as a catalyst for the CH–CH cross-coupling reaction of xanthene with arenes.

Su performed the cross-dehydrogenative coupling (CDC) of oxindoles with arenes and/or thiophenols in the presence of GO as a catalyst for the direct synthesis of 3-aryloxindoles and 3-sulfenylated oxindoles (**Scheme 31**).[190] In this research, small molecules such as tetracene, anthraquinone, 9,10-phenanthrenequinone, and DDQ (2,3-Dichloro-5,6-dicyano benzoquinone) were utilized to simulate the active sites of GO for the reaction (**Figure 5**). Tetracene, anthraquinone, 9,10-phenanthrenequinone, and DDQ (2,3-dichloro-5,6-dicyano benzoquinone), gave 9%, 2%, 32% and 82% yields, respectively. As expected, either DDQ or TsOH·H$_2$O alone showed no reactivity. These experiments indicate that the acidic groups and quinone-type functionalities in GO worked synergistically in promoting the CDC coupling.



Scheme 31: GO-catalyzed the CDC of oxindoles with arenes (2mL) and/or thiophenols (chlorobenzene as a solvent).

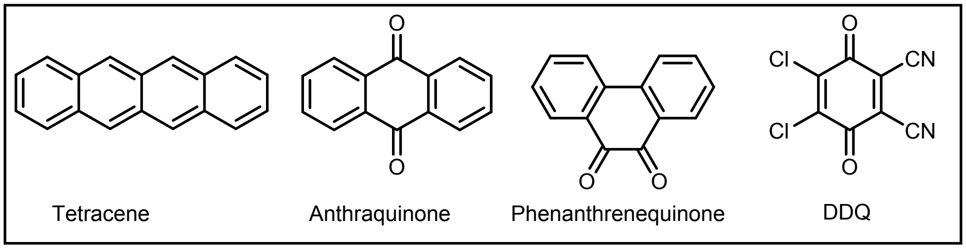
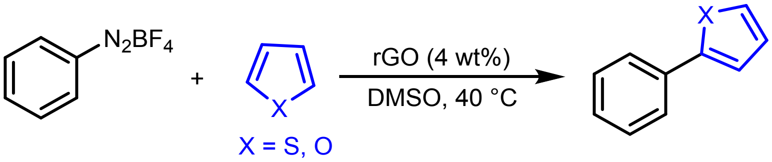


Figure 5: Small molecules as catalysts to confirm the active site for the cross-dehydrogenative coupling of oxindoles with arenes or thiophenols.

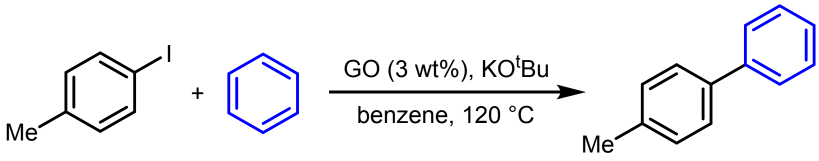
4.4. Miscellaneous reactions

We reported radical coupling between aryldiazonium salts and electron-rich five-membered heterocycles catalyzed by rGO (**Scheme 32**).[178] The reaction provides rapid access to 2-arylfurans, thiophenes, and pyrroles under mild conditions, and the rGO catalysts can be reused several times. The localized radicals on rGO played a vital role in the coupling reaction.



Scheme 32: GO-catalyzed coupling between aryldiazonium salts and five-membered heterocycles.

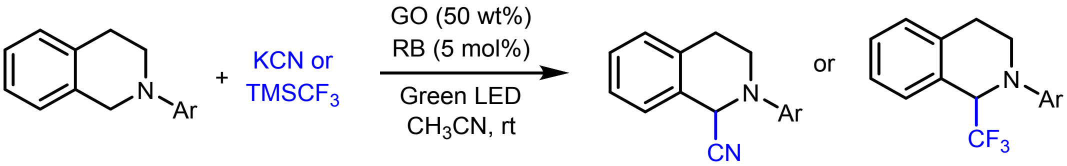
Another inventive coupling for the metal-free synthesis of biaryls involving a free radical mechanism using GO as a catalyst was reported by Wang (**Scheme 33**).[191] In this method, a biaryl compound is formed by reacting benzene with an aryl iodide or bromide in the presence of a strong base. GO showed much higher activity than CNTs, active carbon, carbon black, and natural graphite. Electron-rich aryl iodides are more reactive than those containing electron-neutral or unconjugated substituents. Through mechanistic studies and DFT calculations, it was proposed that the negatively charged oxygen atoms on the GO surface promoted the coupling by activating K^+ ions, next the C−I bond was cleaved to give aryl radical. The reaction of the aryl radical with benzene followed by proton transfer furnishes the biaryl product. The graphene π system facilitates the coupling as the aromatic coupling partners are readily adsorbed through π–π interactions.[187]



Scheme 33: GO-catalyzed biaryl synthesis through radical addition.

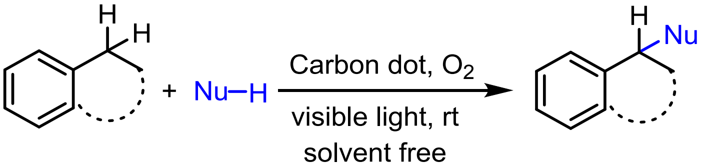
5. Photo absorbed features of carbocatalysts

GO has been reported as a photocatalyst for hydrogen production from water under UV irradiation,[192] and such property of GO was applied for organic synthesis in C−C bond formation. Tan utilized GO and organic dye (RB) as cooperative catalysts for the C−H functionalization of tertiary amines.[193] This methodology avoids the use of metal catalysts and a stoichiometric amount of peroxy-compounds as the terminal oxidant. A cheap and readily available organic dye was used as a cocatalyst, and the air was used as the oxidant (**Scheme 34**). The author proposed that the highly reactive iminium intermediate was formed by the oxidation of the C–H bond adjacent to the nitrogen. RB accepts a photon from the visible light source to populate the excited state (RB*), and remove one electron from the nitrogen atom via a single electron transfer (SET) process. This reaction is specific for GO, but hydrophobic graphite and activated carbon did not affect the rate of reaction.



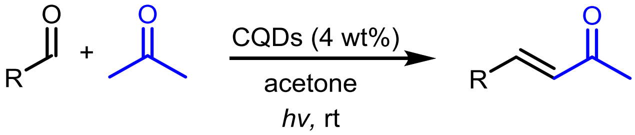
Scheme 34: Photocatalytic coupling reaction using GO and RB as photocatalyst.

Sarma visualized that the combination of photooxidation and surface acidity might be influential in obtaining a high yield of the coupling products in shorter reaction times.[194] The sulfonated carbon dots worked as a catalyst for the cross dehydrogenative coupling of benzylic hydrocarbons with a variety of nucleophilic coupling partners such as ketones, diketones, and arenes by taking advantage of their visible-light-induced photocatalytic and surface acidic properties (**Scheme 35**). The acidic carbon dots demonstrated dual catalytic properties in the photoactivation of benzylic C−H bond in the presence of O_2, resulting in the formation of the hydroperoxy intermediate, followed by coupling with the nucleophiles.



Scheme 35: Carbon dot catalyzed the cross dehydrogenative coupling of benzylic hydrocarbons with a nucleophile.

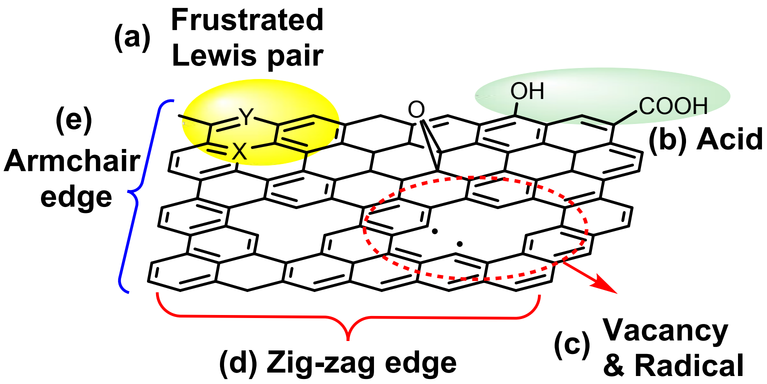
The carbon quantum dots (CQDs) with the size of 5 nm synthesized by an electrochemical etching procedure was employed as photocatalyst for aldol condensations under visible light irradiation (**Scheme 36**).[195] To further confirm the role of the surface hydroxy group of CQDs, deuterated CQDs (CQDs-D) was synthesized and employed as a catalyst for the aldol condensation. Interestingly, hydroxy group free CQDs were found inactive; this suggests that CQDs interact with substrates via hydrogen bonding.



Scheme 36: Carbon quantum dot as a photocatalyst for aldol condensation reaction.

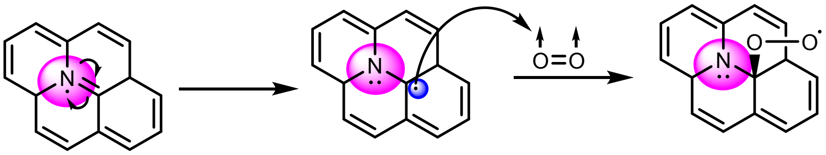
6. Mechanism discussion

The potential of carbocatalysis, one of the major issues in the current state of the art, is the limited understanding of the nature of the active sites responsible for the observed catalytic activity and how this activity and selectivity can be further increased. As shown in the previous sections, GO is the most used graphene-based catalyst. However, GO is very labile; GO is reduced/decomposed under gentle heating (<100 °C) and photo-irradiation even in the absence of reducing reagent.[196,197] In that sense, GO can sometimes be considered as an oxidizing reagent.[121] The active site of graphene-based materials is still not clear; frustrated Lewis pairs (mainly by doping with hetero atoms) (**Scheme 37 (a)**) are reported to be active sites for hydrogenation reactions,[146] acidic sits (**Scheme 37 (b)**) are reported for a series of organic transformations such as reduction reaction,[198] ring-opening reactions,[199] coupling reactions,[4] and many others.[200] Similarly, carbon vacancies (**Scheme 37 (c)**) are reported as active sites for organic transformations such as aerobic oxidation and hydrogenations,[201] and defects in the carbon lattice, zig-zag edge (**Scheme 37 (d)**), and armchair edges (**Scheme 37 (e)**) are considered as active sites for the reduction reactions.[200,202] Carbon materials can possess a lot of unpaired electrons (free radicals), which can withdraw an electron from an electron pair of a molecule to activate the molecule. Hence, free radicals can also be used to catalyze chemicals reactions, more specifically coupling reactions.[203–205]



Scheme 37: Possible active sites on the surface of graphene-based materials.

Combining experiments and theoretical calculations strongly support that the carbon atom vacancies activate the substrate.[206] In addition to the basal plane and defect sites in an sp^2 carbon lattice, heteroatoms can also induce activation of oxygen molecules. The underlying assumption is that the nitrogen or other heteroatoms incorporated in the sp^2 network has an unpaired electron radical that decolonized over the basal plane of graphene, provides possibilities for electron transfer from the neighboring carbon atom to the starting material or reagent (oxygen) (**Scheme 38**).[207]



Scheme 38: Schematic representation of O_2 activation by N-doped graphene.

7. Conclusion and future perspective

Graphene and graphene-based materials have been developed over the last ten years as carbocatalysts, and it is doubtless that such materials can catalyze many liquid phase reactions in organic chemistry. Although the actual mechanisms and the active sites of the carbon catalysts remain issues to be solved, the activity of carbon catalysts may be improved by optimizing the catalyst preparation and reaction conditions.

The intrinsic acidity and basicity of carbon materials as catalysts are related to the oxygenated functional groups or doped heteroatoms. Still, the distribution of acid/base functionalities is not well described in most of the studies reviewed here. More importantly, minor components may have any influence on the catalytic performance. In particular, GO and/or graphene-based materials, which are prepared by the oxidation and reduction of graphite, are generally contaminated by metallic impurities.[208–210]

The most robust methodology for determining the active sites is a combination of theoretical calculations of structure models and in-situ analysis techniques. The GO and graphene-based materials must be characterized thoroughly to confirm functional group distribution, metal contamination, and the presence of radicals, which could be responsible for the catalytic effect. Conclusions that are not based on scientific evidence can undermine the credibility of this area and lead to stagnant research. The importance of replacing metal catalysts with carbocatalysts is universally recognized. To sustainably continue this research in the future, it is necessary to secure credibility and reproducibility in addition to academic novelty. Now that analytical technology has advanced progressively, it has become clear that the catalytic reaction proceeds by the incorporation of ppb level metal species.[211] It may not be necessary to define carbon catalysts as "metal-free" catalysts. A more intense collaboration among synthetic organic chemistry, materials chemistry and physical chemistry could bring about new activities in analysis and catalyst design for improved performance and deeper mechanistic understandings.

Acknowledgment

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