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VIP Carbocatalysis

Graphene Oxide: A Convenient Carbocatalyst for Facilitating Oxidation and Hydration Reactions**

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The incorporation of oxygen into organic substrates using oxidation or hydration transformations is commonly performed using transition-metal-based catalysts that are often expensive, difficult to remove, toxic, and are frequently obtained from limited natural resources.[1] As such, the search for a catalyst that combines the toxicological benefits of a metal-free synthesis with the convenience of heterogeneous workup, whilst retaining high activity, is a continuing effort of critical importance.[1] Herein, we report the use of graphene oxide[2] (GO), a readily available and inexpensive material, as a mild and efficient carbon catalyst for the generation of aldehydes or ketones from various alcohols, alkenes, and alkynes, a process we will refer to as "carbocatalysis".

Historically, GO has functioned primarily as a precursor to reduced graphene oxide (r-GO) or chemically modified graphene (CMG)[3] materials, which have generated a tremendous amount of excitement owing to their remarkable electronic, mechanical, and chemical properties.[4] The synthesis of GO typically involves the oxidation of graphite using either the Hummers ($KMnO_4$ and $NaNO_3$ in concentrated sulfuric acid)[5] or the Staudenmaier ($NaClO_3$ in H_2SO_4 and fuming HNO_3) method.[6] The relatively harsh conditions used in these synthetic protocols introduce a variety of oxygen-containing functionalities (e.g. alcohols, epoxides, and carboxylates) into the material (Figure 1). As a result, GO is slightly acidic (pH 4.5 at 0.1 mg mL^{-1})[7] and has long been recognized as having "rather strong oxidizing properties".[8]

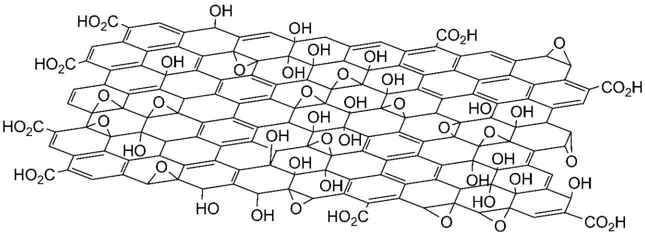
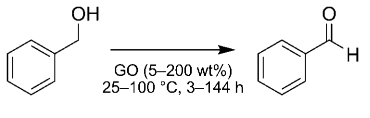


Figure 1. Structural model of graphene oxide (GO) as proposed by Lerf, Klinowski and co-workers.[5b]

Despite this synthetic potential and rich chemical functionality, GO and other CMGs have not been extensively explored as catalysts for facilitating synthetically useful transformations. To date, such efforts have exploited the relatively high surface areas intrinsic to such carbon materials to enhance the activities displayed by supported transition-metal-based catalysts. For example, GO that was impregnated with palladium nanoparticles displayed very high turnover frequencies in Suzuki–Miyaura coupling reactions (approximately 39 000 h^{-1}).[9] Similarly, platinum nanoparticles have also been deposited onto GO for use in methanol electro-oxidation and hydrogen fuel cells.[10]

Independent of these metal-mediated reactions, we are interested in harnessing the inherent reactivity of GO and other graphene-based materials to facilitate useful synthetic transformations, as other carbon allotropes have been recently shown to exhibit fascinating catalytic properties. For example, carbon nanotubes have been shown to dehydrogenate *n*-butane,[11] and C_{60} has been reported to catalyze the hydrogenation of nitrobenzene.[12] Hence, we reasoned that novel reactivities would be observed from carbon catalysts based on the graphene framework, a material with unique electronic and chemical properties, as well as high surface area.[4,13]

In a preliminary experiment, neat benzyl alcohol ($PhCH_2OH$) was heated to 100 °C in the presence of 20 wt% GO[14] for 14 hours under ambient conditions (Scheme 1). Subsequent filtering afforded a mixture of benzaldehyde (PhCHO)/$PhCH_2OH$ in a 1:3 molar ratio, as determined by ^1H NMR spectroscopy; no benzoic acid ($PhCO_2H$) or other by-products were detected under these conditions. To determine whether residual transition-metal-based species were involved in this oxidation reaction, the GO material was analyzed by atomic absorption (AA) spectrometry and inductively coupled plasma mass spectrometry (ICP-MS). In particular, the manganese content[5] was found to be below the detection limit of the AA spectrometer employed (60 parts per billion) and less than 36 parts per billion by ICP-MS (nearly equivalent to other trace metal contaminants found in the material, such as copper, lead, and



Scheme 1. Oxidation of benzyl alcohol using graphene oxide (GO).

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nickel). In further support of a metal-free, carbocatalyzed oxidation process, no reaction was observed when natural flake graphite (used as a starting material to prepare GO) was examined as an oxidant under otherwise identical conditions.

To ascertain the fate of the GO material used in these oxidation reactions, the residual catalyst was separated from the reaction mixture by filtration and characterized. Compared to the GO starting material, the FTIR spectrum (KBr) of the carbon material isolated at the conclusion of the reaction exhibited an attenuated signal (relative to the other peaks in the spectrum) at $\nu = 3150\ \mathrm{cm^{-1}}$ (O–H stretch), as well as the disappearance of diagnostic signals at $1685\ \mathrm{cm^{-1}}$ (C=O stretch), $1280\ \mathrm{cm^{-1}}$ and $1140\ \mathrm{cm^{-1}}$ (attributed to epoxide absorbances[15]). The FTIR spectrum also revealed new signals at $1650\ \mathrm{cm^{-1}}$ and $1500\ \mathrm{cm^{-1}}$, which were attributed to the presence of aromatic and olefinic species. In addition, the isolated material exhibited a significantly higher powder conductivity and C/O ratio than the GO starting material ($15\ \mathrm{S\,m^{-1}}$ versus $2.2\times10^{-5}\ \mathrm{S\,m^{-1}}$ and 7:1 versus 2:1, respectively).[16] Collectively, these results suggested to us that the GO catalyst underwent partial reduction during the conversion of $PhCH_2OH$ into PhCHO and afforded a carbon product that was similar to the r-GOs and CMGs that had been previously synthesized by other methods.[3a,b] This reduction process appeared to be concomitant with the release of water, as determined by NMR spectroscopy and coulimetric Karl Fischer titration of the product mixture.

To determine whether the GO was directly oxidizing the alcohol or functioning as a catalyst with ambient oxygen as the terminal oxidant,[17] the aforementioned oxidation reaction was performed under an atmosphere of nitrogen. After 24 hours at 100 °C, an aliquot removed from the reaction mixture was found to contain less than 5 mol% PhCHO, as determined by NMR spectroscopy. Underscoring the importance of oxygen, continued heating of this reaction mixture under ambient atmosphere afforded 23% conversion into PhCHO after another 24 hours. Notably, upon separation of the catalyst from the substrate by filtration, the GO was found to retain its oxidative properties and was successfully reused for multiple cycles.[18]

To determine if radical species were involved in the aforementioned oxidation processes, neat $PhCH_2OH$ was treated with GO (20 wt%) and butylated hydroxytoluene (BHT; 20 wt%), a known radical inhibitor.[19] After 24 hours at 100 °C, less than 5% conversion into PhCHO was observed by NMR spectroscopy. However, when 1:1:1 (by mass) of GO/$PhCH_2OH$/BHT were heated at 100 °C for 14 hours, a 26% conversion was observed, indicating BHT does not inhibit the ability of GO to oxidize the alcohol to a significant extent, but rather impedes the oxidation of the reduced catalyst. In support of this assessment, heating GO in the presence of cyclopropylcarbinol resulted in the formation of a number of products, including olefinic species, as determined by NMR spectroscopy; no aldehyde or carboxylic acid products were observed. Similar results were obtained when chromic acid was used to oxidize this same substrate, a process known to proceed via radical species.[20]

As summarized in Table 1 (see Table S1 for additional optimization studies), the oxidation properties of GO were studied under various conditions, including catalyst loading (5–200 wt%), temperature (25–150 °C), and reaction time (3–144 h). At temperatures ≤ 75 °C, the percentage conversion peaked at 73%, even after long reaction periods (144 h) and high catalyst loading (200 wt%). However, temperatures above 100 °C were found to increase the conversion of $PhCH_2OH$ into PhCHO to 85%, although relatively high catalyst loadings (≥ 50 wt%) were still required.[21] At elevated temperatures (≥ 100 °C), an appreciable amount of $PhCO_2H$ was observed in the NMR spectra of the reaction mixtures. Moreover, the acid content appeared to increase with temperature, catalyst loading, and reaction time. Ultimately, we found that heating $PhCH_2OH$ in the presence of 200 wt% GO at 100 °C for 24 hours afforded high conversions (> 98%) with good selectivity for the aldehyde versus the acid (92:7).

Table 1: Oxidation of benzyl alcohol into benzaldehyde and benzoic acid under various conditions.[a]

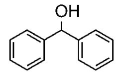
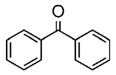
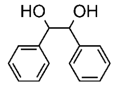
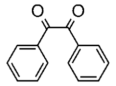
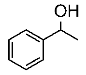
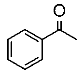
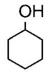
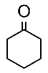
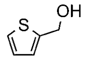
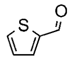
Catalyst[b]	Loading [wt%]	T [°C]	PhCHO [%][c]	$PhCO_2H$ [%][d]	TON ($\times10^{-2}$)[e]
GO	20	100	24	0	1.1
GO[f]	20	100	22	0	1.0
graphite[g]	20	100	0	0	–
GO	5	75	5	0	0.93
GO	5	100	5	0	0.93
GO	5	150	6	0	1.1
GO	20	75	12	0	0.56
GO	20	100	24	0	1.1
GO	20	150	27	0	1.3
GO	50	75	30	0	0.56
GO	50	100	61	0.1	1.1
GO	50	150	85	12	1.6
GO	200	75	73	4	0.36
GO	200	100	92	7	0.43
GO	200	150	49	51	0.46

[a] Unless otherwise noted, all reactions were performed in neat benzyl alcohol using the catalyst loading and temperature indicated for 24 h. [b] Unless otherwise noted, the GO was prepared using the Hummers method.[5] [c] Refers to the conversion of benzyl alcohol into benzaldehyde, as determined by ^1H NMR spectroscopy. [d] Refers to the conversion of benzyl alcohol into benzoic acid, as determined by ^1H NMR spectroscopy. [e] The turnover number (TON) was calculated as a ratio of the mol of oxidized product/mass GO. [f] Catalyst was prepared using the Staudenmaier method.[6] [g] Natural flake graphite was purchased from Bay Carbon, Inc. or Alfa Aesar and used without further purification.

The turnover numbers (TON; expressed as a ratio of mol product produced/mass catalyst because of the non-Berthol-loid nature of the GOs) for the various oxidation reactions were calculated and summarized in Table 1. The measured values remained relatively constant at $10^{-2}\ \mathrm{mol\,g^{-1}}$, irrespective of catalyst loading or reaction temperature, which suggested to us that the catalyst consistently reached its maximal activity under these conditions.

Next, the scope of reactivity of the aforementioned carbocatalyst was explored using a variety of primary and secondary benzylic and aliphatic alcohols under conditions that resulted in the highest conversion of $PhCH_2OH$ into its oxidized products (200 wt% GO, 100 °C, 24 h). As summarized in Table 2,[22] benzylic alcohols (Table 2, entries 1–3)

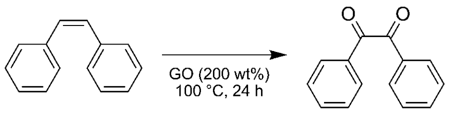
Table 2: Oxidation of various alcohols.[a]

Entry	Alcohol	Product	Conversion [%]
1[b]			> 98
2[b]			96[c]
3[d]			26
4			> 98
5[d]			18

[a] Conditions: 200 wt% GO, 100 °C, 24 h. Conversion of the alcohol into the aldehyde/ketone was monitored by ^{1}H NMR spectroscopy. [b] The solid alcohol substrate was dissolved in a minimum of chloroform to facilitate the oxidation. [c] A small amount of benzaldehyde (2%) was also observed. [d] The reported conversion was determined after 24 h at 75 °C using 50 wt% GO. A mixture of unidentifiable products was observed when the reaction was performed at 100 °C using 200 wt% GO.

resulted in moderate to high conversions into the product. Aromatic groups did not appear to be a constraint, however, as highlighted by the ability of GO to effectively catalyze the oxidation of cyclohexanol (Table 2, entry 4). Notably, a modest conversion of 2-thiophenemethanol into the respective aldehyde was observed to proceed without sulfur oxidation (Table 2, entry 5).[23] This latter result indicates that GO may exhibit broad chemoselectivity and functional group tolerance, and therefore be useful in overcoming such challenges in transition-metal-mediated catalysis.[1]

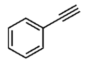
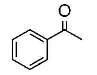
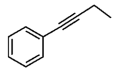
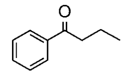
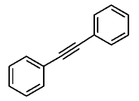
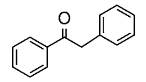
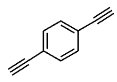
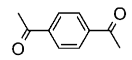
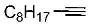
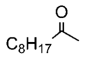
Given the propensity of GO to oxidize various alcohols, efforts were also directed toward exploring the ability of this catalyst to oxidize unsaturated hydrocarbons. As shown in Scheme 2, benzil was isolated in 49% yield (56% conversion by NMR spectroscopy) after 24 hours at 100 °C from treatment of *cis*-stilbene under the optimized conditions; no benzoin or other oxidation products were observed in the crude reaction mixture. The aromatic substituents, combined with a *cis* geometry, appear to be necessary to facilitate oxidation as either isomerization or no reaction was observed when other alkenes (*trans*-stilbene, 3-hexene, cyclohexene, and β-methylstyrene) were explored as substrates under similar conditions. These apparent limitations may be due to steric constraints or to the orientation of the interaction involved between the olefins and the surface of the catalyst.[24]



Scheme 2. Oxidation of *cis*-stilbene using GO. Conversion of the olefin into the dione (56%) was monitored by ^{1}H NMR spectroscopy. The product was isolated in 49% yield.

In contrast to the alkene oxidation reactions described above, treatment of GO with various alkynes under similar conditions afforded their respective hydration products (see Table 3). Good to excellent conversions into their corresponding ketones were achieved, even at relatively low temperatures (100 °C). It has been previously demonstrated that alkynes undergo hydration under acidic conditions, but only at elevated temperatures (200 °C or higher);[25] hence, we surmised that the observed reactivities were due to the acidic nature of GO. Regardless, the conversions of these reactions are equal to or higher than other non-metal-mediated alkynyl hydrations and proceeded under comparatively mild conditions.

Table 3: Hydration of various alkynes.[a]

Entry	Alkyne	Product	Conversion [%]
1			> 98
2			52
3			41
4[b]			26
5			27

[a] Conditions: 200 wt% GO, 100 °C, 24 h. Conversion of the alkyne into the hydrate was monitored by ^{1}H NMR spectroscopy. [b] The mono-oxidized product 1-(4-ethynylphenyl)ethanone (24%) was also observed.

Despite the relatively high catalyst loadings used in many of the aforementioned reactions, the use of GO may be justified on its cost (less than USD 1 g^{-1}) and convenience. For example, tetrapropylammonium perruthenate (TPAP; an active aerobic ruthenium oxidation catalyst[26]) exhibits a oxidation TON of 0.40 (expressed as a mol/mass ratio) for a variety of alcohols, but is relatively expensive (over USD 120 g^{-1} from Strem Chemicals). When normalized for cost, TPAP gives a lower TON per dollar than GO (3×10^{-3} versus 1×10^{-2}, respectively), revealing the latter to be economical. Moreover, the spent carbocatalyst can be recovered at the end of the reaction and reused by the oxidation methods described above.

In summary, GO was demonstrated to catalyze the oxidation of various alcohols and *cis*-stilbene, and the hydration of various alkynes. These reactions were found to proceed under relatively mild conditions and afforded the desired product (aldehyde, acid, or ketone) in good to excellent yields. Moreover, catalyst recovery was found to be both convenient and effective using simple filtration techniques. To the best of our knowledge, these results constitute the first examples of using graphene-based materials as (metal-free) carbocatalysts to facilitate synthetically useful transformations. In a broader perspective, the promise of GO and other 2D arrays of carbon materials now extends beyond the utilization of their remarkable electronic and mechanical properties.[4]

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[14] The GO employed as a catalyst for these studies was prepared from natural flake graphite using the Hummers method;[5] however, similar results were obtained when GO was prepared using the Staudenmaier method (see Table 1).[6]

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[16] The BET surface area of the GO starting material ($0.7\,m^2g^{-1}$) was similar to that measured for the reduced product obtained after the oxidation reaction ($3.2\,m^2g^{-1}$).

[17] In a related study, carbon molecular sieves were shown to facilitate 40, 46, and 48 % conversions of 1-propanol, 2-propanol, and propanal into mixtures of their corresponding aldehyde, ketone, and alkene at 230 °C in a flow reactor. See: G. C. Grunewald, R. S. Drago, *J. Am. Chem. Soc.* **1991**, *113*, 1636–1639.

[18] At high initial loadings (≥ 50 wt %), no change in activity was observed for up to 10 cycles. However, at low catalyst loadings (≤ 20 wt %), the recovered catalyst exhibited only approximately 5 % conversion of $PhCH_2OH$ into PhCHO after 24 h at 100 °C. Hence, as the alcohol oxidation reaction proceeds, the catalyst may undergo reduction to a point such that reversion to GO is no longer favored under ambient conditions.

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[21] Conversion appeared to plateau within 6 hours under these conditions, indicating that catalyst deactivation may be occurring, primarily by thermal reduction. See: Y. Zhu, M. D. Stoller, W. Cai, A. Velamakanni, R. D. Piner, D. Chen, R. S. Ruoff, *ACS Nano* **2010**, *4*, 1227–1233. In support of this hypothesis, the use of chemically reduced graphene oxide (prepared by reduction of GO with hydrazine hydrate[3a]) as the catalyst showed no oxidative products when treated with $PhCH_2OH$ under conditions similar to those described above.

[22] In some of the oxidation reactions described, the initial heterogeneous dispersion stabilized upon heating/stirring. The respective catalyst was conveniently separated by dissolution of the product mixture in methylene chloride or chloroform, followed by filtration of the precipitated solids. There was no loss of the carbon content of the employed catalyst during the reaction, based on elemental analysis data; however, the total mass of the catalyst decreased as it lost a portion of its oxygen functionality and was reduced.

[23] Similarly, benzylamine was converted into benzaldehyde (28 % conversion; conditions: 50 wt % GO, 75 °C, 24 h). Presumably, the reaction proceeded through the respective imine, which underwent rapid hydrolysis. In contrast, 1-butanol, allyl alcohol, 2-mercaptoethanol, and 2-(methylthio)ethanol showed little or no conversion into their oxidized products under any of the conditions tested.

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