

Catalysis

Nanosized Copper Supported on Graphene as Catalyst for the Oxidative C–O Cross-Coupling of Phenols

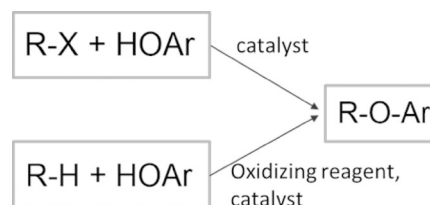
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Copper nanoparticles prepared by the polyol reduction method have been supported on graphene and the resulting Cu/G catalyst used for the oxidative C–O cross-coupling of o-substituted phenols and N,N-dialkylformamide to the corresponding carbamates. The presence of B or N dopant elements on graphene plays a negative effect on the catalytic activity of resulting Cu supported catalyst. The advantage of using graphene as support is illustrated by the superior catalytic activity of Cu/G compared to Cu supported on single walled carbon

nanotubes, diamond nanoparticles, active carbons and acid (TiO₂ and CeO₂), neutral (Al₂O₃) and basic (MgO) metal oxides. Cu/G catalyst was recovered and reused without observing variations in the time-conversion plots of the reaction. Moreover, the catalyst is also efficient for the coupling of ethers and aldehydes. The scope of Cu/G as catalyst for the oxidative C–O coupling includes other related aromatic and non-aromatic compounds.

Introduction

Metal catalyzed cross-coupling reactions to form C–C and C–X (X: N, O, S) bonds have become very versatile processes in organic synthesis due to the high yields that can be achieved, its compatibility with a large range of functional groups and mild reaction conditions.^[1,2] In many of these reactions, aryl halides are the substrates and the new bond is formed by replacement of the C–halide bond. For the sake of atom economy and convenience of the starting materials, it would be desirable to perform cross-coupling reactions by activation of C–H without the need of using organic halides as reagents. C–H bonds can be activated in cross-coupling reactions by using suitable oxidizing reagents, leading to the oxidative version of the cross-coupling process (Scheme 1). Pd salts and complexes are the most general catalysts for both versions of cross-coupling reactions, either using aryl halides as starting materials or coupling by oxidative activation of C–H bonds.^[3] A general tendency in catalysis is to replace costly precious metals, and Pd in particular, by more abundant and affordable first row transition metals. Thus,



Scheme 1. Two possible versions of C–O cross-coupling reaction by using an aryl halide or by oxidative C–H activation.

there is still room for developing catalysts for cross coupling reactions.

There are some precedents in the literature showing that Cu under certain conditions can catalyze some types of Ullmann, C–X cross-couplings between aryl iodides and amides, thiols or phenols.^[4] Besides the use of soluble metal species, the use of metal NPs supported on a suitable large surface area material is a general strategy to develop heterogeneous, reusable catalysts.^[5] Most of the studies on supported metal NPs have used metal oxides, either amorphous or porous to deposit the active metal species.^[6] Besides metal oxides, active carbons have been among the preferred solids to develop heterogeneous catalysts based on supported metal NPs.^[7] More recently, with the advent of graphene (G) and related materials, there has been large interest in exploiting the properties of these carbon nanoforms as support of metal NPs.^[8] G is constituted by a one atom thick layer of sp² carbons in hexagonal arrangement. G as support offers several advantages including large specific surface area and tuning of the catalytic activity of the supported metal by overlapping of the extended π orbital of graphene with the d orbitals of the metal atoms at the interface. This π -d orbital overlap can modify the electronic density of the metal atoms of the supported NPs. In addition, G has

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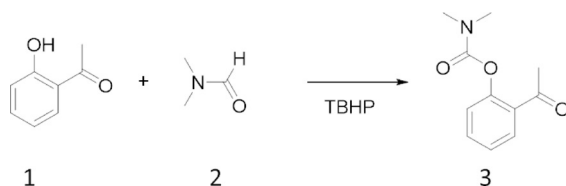
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a high adsorption capacity that can be useful to bring substrates and reagents in close proximity to the active metal NPs. We recently reported an efficient methodology for the synthesis of graphene materials from biomass waste. Pyrolysis treatment of a series of biopolymers including alginate, chitosan and carragenan affords graphene or N-, B-, and S-doped graphenes that have been successfully used as metal-free catalysts in a variety of organic transformations.^[9,10]

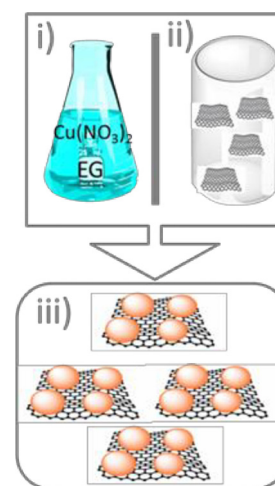
In the present manuscript, we report the activity of Cu NPs supported on G (Cu/G) as catalyst for the oxidative coupling of o-hydroxyacetophenone and (ph)enolic OH groups with dimethyl and diethylformamides promoted by t-butylhydroperoxide (TBHP) to form the corresponding aryl substituted carbamates (Schemes 2 and 4). This coupling reaction has the advantage of not needing halogenated starting materials, and the use of widely abundant Cu as catalyst. Our report moreover illustrates the advantages of graphene as support with respect to other carbon solids or inorganic metal oxides.



Scheme 2. Oxidative cross-coupling of o-hydroxyacetophenone (1) and N,N-dimethylformamide (2) promoted by TBHP.

Results and Discussion

In the first stage of our work, a catalyst based on Cu NPs supported on G (Cu/G) was prepared and characterized. Cu NPs were obtained starting from $\text{Cu}(\text{NO}_3)_2$ as a precursor by reduction in hot ethylene glycol. The polyol method in which a metal salt is reduced in a viscous polyol media has become a general methodology to prepare metal NPs with narrow particle size distribution about 5–10 nm.^[11] The G samples used in the present study were obtained by pyrolysis at 1000 °C under inert atmosphere of natural alginate and subsequent exfoliation of the resulting turbostratic graphitic carbon residue by sonication in water following a procedure previously reported.^[9b] Deposition of Cu NPs on G was carried out by adding a suspension of G in water to ethylene glycol in which previously Cu NPs have been formed as visually observed by the red color developed during the process. The relative weight of $\text{Cu}(\text{NO}_3)_2$ and G were adjusted to prepare samples with a nominal Cu content about 2 wt. %. Scheme 3 summarizes the steps followed in Cu/G preparation. Analogously, other Cu catalysts in which Cu was supported on different carbon materials such as N-doped G, active carbon (AC), single wall carbon nanotubes (SWCNTs) and diamond nanoparticles (D NPs) or inorganic metal oxides (Al_2O_3 , TiO_2 , MgO , CeO_2) were also prepared. The experimental section describes the origin, pretreatment and main textural and physicochemical parameters of these supports, and Table 1 contains analytical data of these supported Cu catalysts. Cu/G was characterized by analytical, spectroscopic and imaging techniques.



Scheme 3. Cartoon illustrating the preparation of Cu/G. i) Formation of Cu NPs by boiling $\text{Cu}(\text{NO}_3)_2$ in ethylene glycol (EG); ii) Preparation of G suspended in water by sonication of carbonaceous residues from pyrolysis of alginate at 900 °C; iii) Deposition of Cu NPs on Gs.

Table 1. Main textural and analytical data of the catalysts used in the present study.

Catalysts	Surface area (m ² /g)	Particle size (nm)	Cu content (wt %)
(N)G	1500	35	1.6
Active carbon (AC)	1140	6	1
SWCNTs	20	-	0.7
DNPs	250	8	0.5
Al_2O_3	70	20	1.6
TiO_2	60	25	1.7
MgO	80	4	1.85
CeO_2	180	5	1.8

The Cu content of the samples was 1.6 wt% as determined by ICP analysis after digestion of the samples with concentrated nitric acid. Raman spectroscopy shows the characteristic 2D, G and D bands expected for defective graphene appearing at 2700, 1600 and 1380 cm^{-1} , respectively. The relative intensity of the G vs D band (I_G/I_D) was 1.3 that indicates the presence of some defects on the G sheet due to oxygenated functional groups. It has been reported that I_G/I_D ratio can be used to quantify the relative population of defects.^[12] In some of these precedents describing the preparation of reduced graphene oxide, I_G/I_D ratios of about 0.8 have been measured. Therefore, the value of I_G/I_D indicates that although our G sample has oxygenated functional groups, their density is lower than other samples that have been used in previous works reporting the use of G as support of metal NPs. The presence of Cu and its oxidation state can be addressed by observing in Raman spectroscopy the presence of weak vibrations bands at 850 and 435 cm^{-1} for Cu_2O and 590 cm^{-1} for CuO , respectively. The weakness of these bands is due to the low Cu loading in Cu/G. It is worth noting that observation in Raman spectroscopy of the bands corresponding to Cu_2O and CuO constitutes firm evi-

dence that Cu NPs undergo partial oxidation upon sample storage at the ambient.

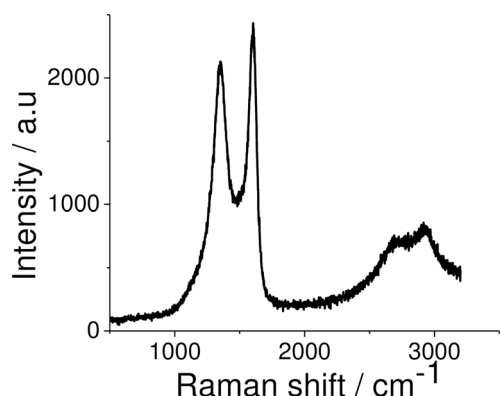


Figure 1. Raman spectrum recorded for Cu/G showing the characteristic bands of defective G.

The presence of Cu and O in Cu/G was also observed in XPS spectroscopy. Figure 2 shows the high resolution Cu2p and

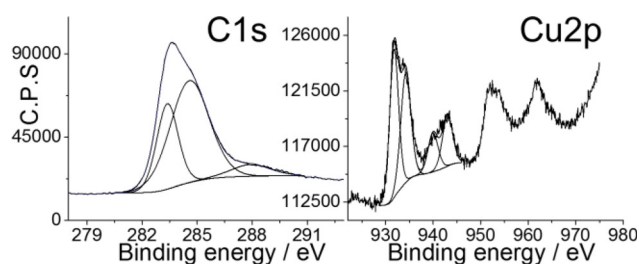


Figure 2. High resolution C1 s (left) and Cu2p (right) XPS peaks recorded for Cu/G as well as their best deconvolution to individual components.

C1 s peaks as well as the best deconvolution to their individual components according to the literature. Thus, as it can be seen in this Figure 2, the Cu2p has two components of relative atomic contribution of 0.65 and 0.6 at % corresponding to Cu (I) and Cu (II), respectively. C1 s, on the other hand, shows as expected, a major contribution of graphenic C sp^2 (73%) accompanied by 5.8% of C sp^3 present at defects of the G sheet.

The layer morphology of Cu/G and the presence of Cu NPs on the sample was confirmed by microscopy techniques. Figure 3 shows selected TEM images of Cu/G samples as well as the histogram corresponding to Cu NPs distribution. It can be seen there that the sample contains a few large Cu NPs, together with a larger number of small Cu NPs that are well distributed throughout the G sheet. After characterization, Cu/G was evaluated as catalyst for the oxidative coupling of o-hydroxyacetophenone (**1**) in DMF promoted by TBHP. The only product observed in all cases was the corresponding o-(2-acetylphenyl)-N,N-dimethylcarbamate (**3**). It was observed that pretreatment of Cu/G with hydrogen at 200 °C just before its use for the oxidative coupling was remarkably beneficial from

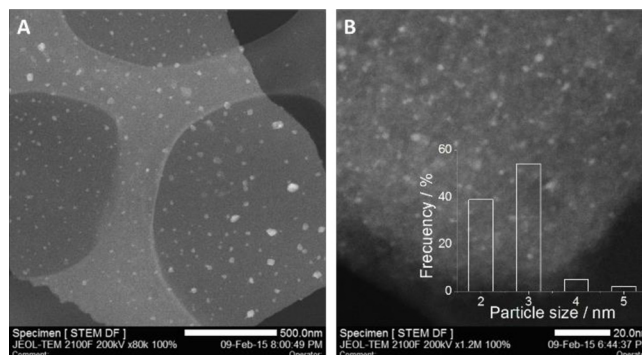


Figure 3. Dark field TEM images at two different magnifications taken for Cu/G. The inset of panel B shows the histogram with the particle size distribution for Cu NPs.

the point of view of the catalytic performance (Figure S.1). The benefits of hydrogen activation can be easily rationalized considering that ambient storage of Cu/G should result in the formation of a large percentage of copper oxides, as previously commented based on X-ray photoelectron spectroscopies, and that the hydrogen treatment should reduce part of these copper oxides to lower oxidation states. Considering that commercial TBHP can be dissolved in different solvents, a comparison in the catalytic activity of TBHP in water and decane was made showing that water is the most adequate co-solvent to perform the reaction in DMF (Figure S.2). The influence of the amount of TBHP and the procedure of its addition, either at the beginning of the reaction in a single aliquot or periodically during the course of the reaction, was determined in a series of experiments (Figure S.3) reaching the conclusion that 4 eq. of TBHP dosed at initial reaction time is an adequate amount to obtain an optimal conversion of **1** and higher yield of **3**. In other series of experiments the amount of Cu/catalyst was also optimized in the range of 0.05 to 2 mol % Cu, finding that 0.5 mol % is sufficient to reach complete conversion in 1 h reaction time under general reaction conditions.

The influence of G as a support and particularly the influence of dopant elements on G was assessed by comparing under optimized conditions (1 mmol of **1**, 1.2 mL of DMF, 4 eq. of TBHP and 0.5 mol % Cu) for a series of four G samples, two of them prepared by pyrolysis of alginate [G and (B)G] and two more obtained by pyrolysis of chitosan [(N)G and (B,N)G]. Two of the samples use borate as a source of boron atoms that under the pyrolysis treatment becomes incorporated into the G structure leading to B doped Gs [(B)G]. When the precursor of G was chitosan, a natural oligosaccharide of glucosamine, the resulting G becomes doped with N [(N)G]. If chitosan is modified by boric acid, then a B,N-codoped G is obtained [(B,N)G]. Preparation and characterization of (N)G, (B)G and (B,N)G has been already reported in the literature and convincing evidence of doping has been presented by Raman and XP spectroscopy.^[8a,13,9,14] The doped G samples used as supports of Cu NPs show coincidence XP spectra as those reported in the literature for these samples. Specifically, these XP spectra show the presence of a peak of the corresponding dopant element and

deconvolution of the experimental peak of the heteroatom into individual components shows the presence of three (in the case of N) or two (in the case of B) components corresponding to graphitic dopant element or dopant element incorporated into the G sheet and bonded to oxygen atoms.

These doped Gs were also used as support of Cu NPs that were deposited as previously indicated in a Scheme 3. The catalytic data shows that the presence of N atoms either as dopant or co-dopant element was highly detrimental for the activity of the resulting Cu catalyst, while (B)G as support renders a catalyst with similar, but lower, activity than G. The time conversion plots for the series of Cu catalyst supported on doped G are presented in Figure 4. Thus, Cu/G was the most active

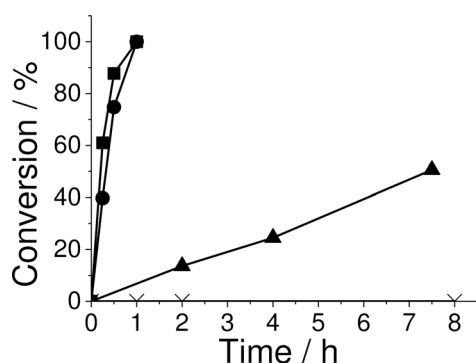


Figure 4. Time conversion plots for the oxidative C–O coupling of o-hydroxyacetophenone and DMF. ■) Cu/G; ●) Cu/(B)G; ▲) Cu/(N)G; x) Cu/(B,N)G. Reaction conditions: 2-hydroxyacetophenone (1 mmol), 2 ml of DMF, 4 eq of TBHP in decane and 0.5 mol % of Cu/G or doped G for 1 h at 80 °C.

catalyst of the series. As commented in the introduction the electronic density of metal NPs can be altered by the presence of dopant elements on G. In the present case it seems that this alteration of the electronic density, particularly by the presence of N atoms, plays a negative role on the catalytic activity. It could be that the higher electronic density introduced by some N atoms tend to stabilize Cu oxidation states that are not acting as active sites. In the literature, there are precedents in which the catalytic activity of N-doped G as support of metal NPs was also found lower than that of G.^[8a]

In heterogeneous catalysis it is a well-known fact that the nature of the support can play a strong influence on the catalytic activity of the active supported NPs through various effects including modulation of the electronic density of the metal atoms and cooperation to the mechanism by adsorption of substrates and reagents near the sites.^[15] Continuing with the influence of the support on the catalytic activity of Cu NPs during the oxidative coupling of o-hydroxyacetophenone and DMF, the activity of Cu NPs supported on other carbonaceous materials and metal oxides was also evaluated. Metal oxides have been among the preferred solid supports for metal NPs due to their stability, large surface area and the possible presence of active sites. These experiments were carried out trying to use samples at similar Cu loading (see loading in Table 1) and keeping constant the 1-Cu molar ratio. The results ob-

tained are summarized in Figure 5, where the catalytic activity of Cu/G has also been included for comparison. As it can be

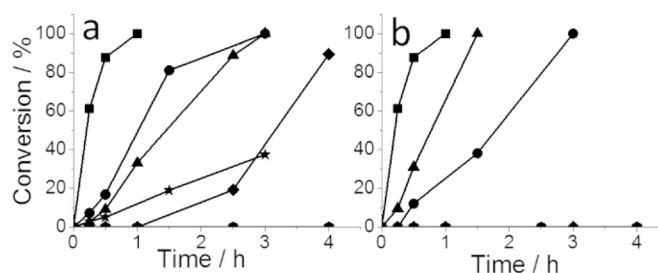


Figure 5. Time-conversion plots for the C–O coupling of 1 and DMF catalyzed by Cu catalysts; a) ■ Cu/G; ● Cu/CeO₂; ▲ Cu/Al₂O₃; ★ Cu/TiO₂; ◆ Cu/MgO; ● G; b) ■ Cu/G; ● G; ▲ Cu/SWCNTs; ● Cu/AC; ◆ Cu/D. Reaction conditions: 2-hydroxyacetophenone (1 mmol), 2 ml of DMF, 4 eq of TBHP in decane and 0.5 mol % of catalyst for 1 h at 80 °C.

seen in this Figure 5, Cu/G was again considerably more active than Cu supported on active carbon, SWCNTs, and on diamond NPs (Figure 5a). Not only that, Cu/G was also more efficient than Cu NPs supported on acidic (CeO₂ and TiO₂), neutral Al₂O₃, or basic (MgO) metal oxides supports (Figure 5b). It was observed that the use of MgO leads to the lowest active catalyst of the series exhibiting an induction period of about 1 h. Although the available data indicates the pivotal role played by the G support imparting Cu catalyst with the highest activity, it is clear that comparison among catalysts that differ in surface area, particle size and, in the case of SWCNT and diamond NP even Cu loading, have to be taken cautiously. Other Cu containing catalysts that were also tested were commercial Cu₃(BTC)₂ (BTC:1,3,5-benzenetricarboxylate, Basolite C) that was able to promote some decomposition of TBHP, but without the formation of the coupling carbamate product. In precedents in the literature the superior performance of G as support of metal NPs has been attributed to a combination of factors including large surface area, high absorption capacity of substrates and reagents and strong metal-support interaction derived from the overlap of the d orbitals of the metal with the extended π orbitals of G.^[8a] Thus, the activity data presented here can be rationalized in the same way and would constitute an additional example of the superiority of G as support of metal NPs in catalysis.

The catalytic activity of Cu/G was also compared to that of Cu(NO₃)₂ as homogeneous catalyst. Cu(NO₃)₂ was fully soluble in DMF under the reaction conditions. It was observed that Cu/G was also more active as a catalyst than the dissolved Cu salt that also exhibited activity for the oxidative coupling, but with a significantly lower initial reaction rate.

The influence of the reaction temperature in the range from 60 to 80 °C was also studied, observing that the initial reaction rate increases along the reaction temperature. This expected influence of the reaction temperature on the catalytic activity of Cu/G allows obtaining the apparent activation energy by plotting the natural logarithm of the reaction rate constant vs the reciprocal of the absolute temperature. The esti-

mated E_a was 43.6 kJ/mol, which is a value that is not uncommon compared to other metal catalyzed oxidative couplings.

Reusability of the catalyst was studied by performing a consecutive series of reactions in which Cu/G was recovered by filtration washed with DMF, re-suspended by sonication and used for a new run with fresh starting materials. Figure 6 shows the

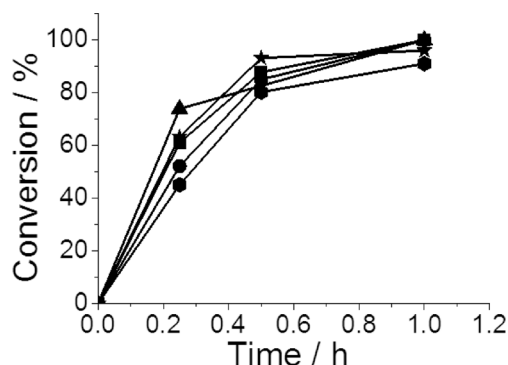


Figure 6. Time-conversion plots for the oxidative coupling of **1** with DMF using Cu/G as catalyst for five consecutive runs. ■) R_0 ; ●) R_1 ; ▲) R_2 ; ★) R_3 ; ◆) R_4 ; Reaction conditions: 2-hydroxyacetophenone (1 mmol), 2 ml of DMF, 4 eq of TBHP in decane and 0.5 mol % of Cu/G or doped G for 1 h at 80 °C.

time conversion plots for this study of catalyst recycling. The time conversion plots of five consecutive uses show a gradual deactivation of the catalyst, as determined by the gradual but marginal decrease of the initial reaction rate from $0.86 \text{ mol/L} \times \text{h}$ to $0.80 \text{ mol/L} \times \text{h}$ and the decrease in the yield of product **3** at final reaction time from 95 to 85%. These variations are, however, minor considering the difficulty in the complete catalyst recovery and the need to adjust reagent amounts and concentrations to the recovered catalyst weight.

The scope of Cu/G as catalyst for the oxidative dehydrogenative coupling was screened for a series of phenols and formamides. Figure 7 shows representative time-conversion plots

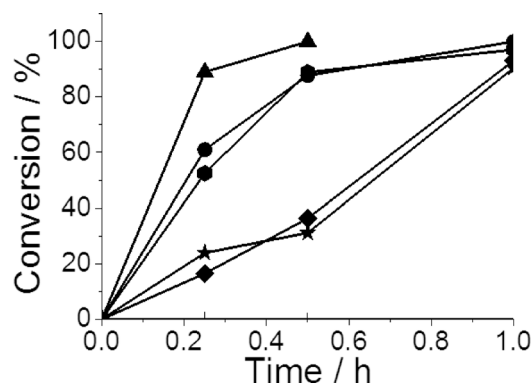
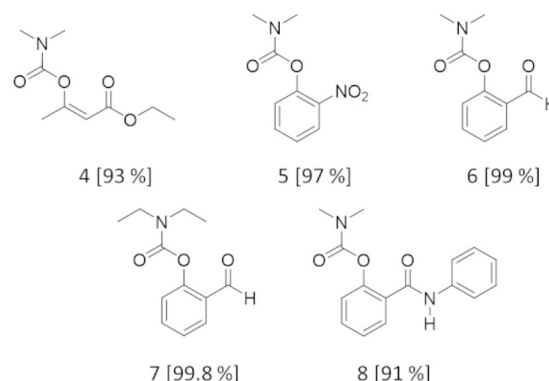


Figure 7. Time-conversion plots for the oxidative coupling of a series of substrates having active O–H groups and formamides: ●) dimethylformamide; ▲) diethylformamide; ★) salicylanilide; ◆) ethyl acetoacetate; ■) 2-nitrophenol; +) 2-ethoxyphenol; Reaction conditions: formamide (1 mmol, 2 mL), Cu/G (0.5 mol %), 4 eq TBHP in decane.

for different reactions and the reaction products are drawn in Scheme 4. As it can be seen there, good yields of the expected coupling product were obtained in all cases. Thus, it was ob-



Scheme 4. Products formed in the oxidative C–O coupling of various substrates catalyzed by Cu/G. The final yields are indicated in brackets. Reaction conditions: substrate (1 mmol, 2 mL), Cu/G (0.5 mol %), 4 eq TBHP in decane.

served that diethylformamide reacts faster than DMF and the reactivity of *o*-nitrophenol is similar to that of **1**. The enol of ethyl acetoacetate can also undergo oxidative coupling similar to phenols and salicylanilide was also reactive. Similarly, dioxane can also be coupled with **1** using TBTH as oxidant reaching very high yields at final reaction times (Figure 8). The oxidative

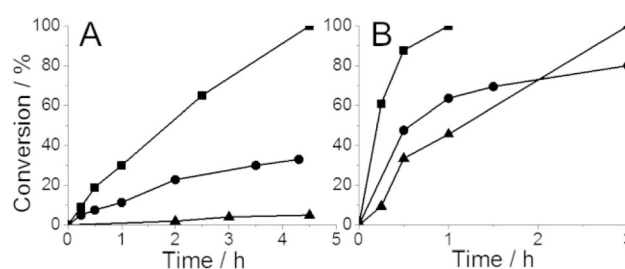


Figure 8. Time-conversion plot for the C–O coupling between *o*-hydroxyacetophenone and A) dioxane or B) benzaldehyde at different temperatures. ▲) 80 °C; ●) 90 °C; ■) 100 °C. Reaction conditions: 2-hydroxyacetophenone (1 mmol), 2 ml of A) dioxane or B) benzaldehyde, 4 eq of TBHP in decane and 0.5 mol % to 1 mol % of Cu/G at 100 °C.

coupling also results in the expected product using benzaldehyde as starting material. Figure 8 shows time conversion plots for the coupling of dioxane and benzaldehyde.

With regard to the oxidation mechanism, we propose that the reaction follows a similar pathway to that previously proposed for this reaction that may involve the coupling of phenoxy and $\cdot\text{CONMe}_2$ radicals generated from phenol and formamide, respectively, by hydrogen abstraction of O-centred radicals derived from TBPH. Accordingly, the main role of the Cu catalyst would be activation of TBPH and formation of the primary radicals ^[3].

Conclusions

In the present study, it has been shown that G is a suitable support of Cu NPs leading to a reusable catalyst that can promote the oxidative coupling of substituted phenols and compounds with acidic OH groups with formamides. The reaction requires TBPH in moderate excess to occur. The presence of heteroatoms on G, particularly N atoms, is detrimental for the catalytic activity of the resulting Cu catalysts. G as a support provides a catalyst that is more efficient than analogous Cu catalysts on other type of carbons and metal oxides or even more active than homogeneous soluble Cu salts. Cu/G succeeded also in performing challenging couplings starting from ethers and aldehydes thereby expanding the library of functional substrates accessed through this route. The observed activity of Cu/G illustrates again the potential that G offer as a support of metal NPs in heterogeneous catalysis.

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Keywords: Graphene as support • graphene supported Cu nanoparticles • oxidative cross-coupling • C–O cross-coupling

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