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"Copper-in-charcoal" revisited: delineating the nature of the copper species and its role in catalysis

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"Copper-in-Charcoal" Revisited: Delineating the Nature of the Copper Species and Its Role in Catalysis

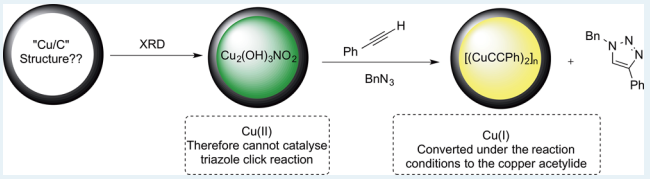
Benjamin R. Buckley,* Rachel Butterworth, Sandra E. Dann, Harry Heaney, and Emma C. Stubbs

Department of Chemistry, Loughborough University, Loughborough, Leicestershire, LE11 3TU, U.K.

Supporting Information

ABSTRACT: "Copper-in-charcoal" has been shown to be a versatile catalytic source of supported copper for a variety of important synthetic transformations, as well as in other fields such as energy. We herein report the characterization of this material and the implications that its preparation has on catalysis, thus providing a greater understanding of the scope and limitations of this catalyst system.

KEYWORDS: *copper, charcoal, triazole, click, heterogeneous*

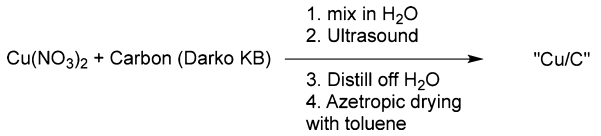


Over the past few decades, a range of catalysts have been heterogenized onto solid supports (e.g., SiO_2, Al_2O_3, mol sieves, etc.), and activated carbon is one of the most commonly employed.[1] These heterogeneous catalysts have received much attention due to their notable increase in reactivity and recyclability when compared to traditional transition-metal-based catalysts.[2] However, research in this area has been largely focused on applying the heterogeneous catalyst systems to a variety of applications rather than characterizing and improving them, probably due in part to the expertise in the research groups reporting the work lying toward organic synthesis rather than materials characterization.[3]

The Lipshutz group, has pioneered the use of metal-based catalysts on carbon supports, for example, Ni/C,[4] Ni/Cg,[5] Cu/C,[6] and mixed metal systems,[8] for a variety of reactions. In particular, they have used copper nanoparticles supported within the pores of activated carbon to act as a source of copper(I) or (II) for a range of heterogeneously catalyzed reactions. Oxidized copper nanoparticles on activated carbon have also been used in CuAAC reactions.[9]

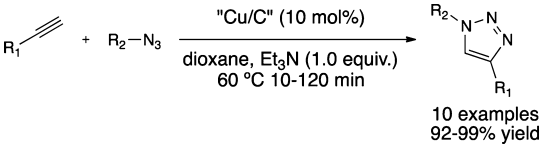
Several different protocols have been reported for the preparation of Cu/C catalysts. For example, Mehandjiev reported a procedure in which the final step involved the copper-in-charcoal material being calcined at 503 K for 2 h,[10a] a similar procedure was reported by Liu with heating at 523 K[10b] and Wey reported the heating of the copper-in-charcoal material at >700 K before the material was analyzed:[10c] all three groups report X-ray powder diffraction data showing the presence of CuO with lesser amounts of Cu_2O in the charcoal matrix. The material prepared and used by the Lipshutz group involved the combination of activated carbon (Darco-KB) and an aqueous solution of copper(II) nitrate using sonification, distillation of water followed by azeotropic drying with toluene to afford the catalyst (Scheme 1).[6a,b] Transmission electron microscopy (TEM) was also used to record 2D images of the carbon material, from which the group proposed a relatively even distribution of the copper nanoparticles within the charcoal matrix;[6b] lastly, quantitative inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to determine the loading of copper within the charcoal, which was found to be 0.344 mmol Cu/g catalyst, as well as the extent of copper bleed into solution during the reactions.[6b] Importantly, we noted that leaching of copper(II) from the carbon matrix was reported during azide formation,[6d] and under flow conditions.[7]

Scheme 1. Lipshutz's Preparation of "Copper-in-Charcoal"



Of particular note, Lipshutz was able to show that high yields in a series of copper assisted Huisgen [3 + 2] cycloaddition reactions could be obtained (Scheme 2). They also showed that the copper-in-charcoal material was particularly robust and were able to use a wide range of solvents using high temperature microwave conditions, with no solubility issues. The catalysts could also be reused (for at least three catalytic cycles) without loss of activity.[6a]

Scheme 2. Lipshutz's "Copper-in-Charcoal" Catalyzed Triazole Click Reaction



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Our multidisciplinary group is interested in the use of heterogeneous catalysts for a variety of applications, and we have previously investigated the role of copper(II) compounds as precatalysts in copper alkyne azide cycloaddition (CuAAC) reactions.[11] In those reactions, the copper(II) species act as a catalyst in Glaser coupling reactions and is thereby reduced to copper(I) with concomitant formation of copper(I) acetylides which are subsequently involved in catalysis of the CuAAC reaction.[11a,c,12] A dicopper(II)-substituted γ-keggin silcotungstate has been used in Glaser coupling reactions[13] and is also reduced to act as a precatalyst in CuAAC reactions.[14] Copper(I) acetylides can also be useful for the A^3 multicomponent synthesis of a range of tertiary amines,[15,16] and they are also involved in the ligand accelerated Stephens–Castro coupling of terminal alkynes and aryl iodides[17a] and Sonagashira–Hagihara reactions.[17b]

We decided to use the versatile supported copper system and initiated the synthesis of the copper-in-charcoal material following the Lipshutz protocol, outlined in Scheme 1. The preparation went as expected, and we obtained a black powder, which we analyzed using X-ray powder diffraction, in order to confirm its identity before use (Figure 1). Previous reports[6a,d]

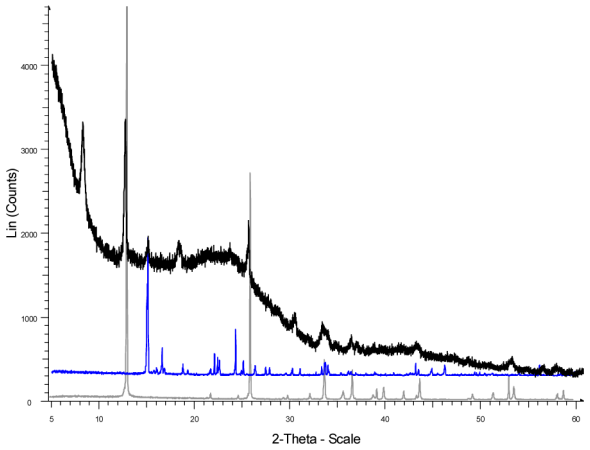
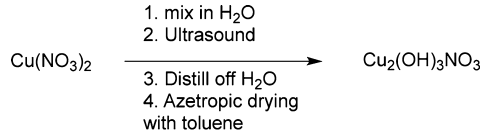


Figure 1. XRD results for the copper-in-charcoal material (top) compared to copper nitrate starting material (blue) and $Cu_2(OH)_3(NO_3)$ (gray).

assumed, as a result of earlier work,[10] that the Cu/C catalyst was a mixture of CuO/Cu_2O bound to the surface of the carbon support: instead we found that the mineral Gerhardite ($Cu_2(OH)_3NO_3$) had been formed as a distinct material, not bound to the support. We then became aware that the copper-in-charcoal material was commercially available,[18] and we decided to analyze that material in order to compare it with our initial material. The two materials were found to match each other; both contained a quantity of copper(II) hydroxynitrate, with a small amount of an unidentified impurity: the impurity was not present when we prepared Gerhardite on Norit A SUPRA as the carbon support, or by omitting the carbon from Lipshutz's procedure for "Cu/C" formation (Scheme 3)

In order to prove that this impurity did not arise from the copper nitrate starting material, a series of reactions were carried out to prepare the copper-in-charcoal (Darco-KB) with a higher loading of copper, where the copper nitrate loading was increased to 2×, 5×, and 10× from the original reaction. The X-ray powder diffraction patterns of the solid support materials prepared in this way are shown in Figure 2.

Scheme 3. Gerhardite Formation Using Lipshutz's Conditions Omitting the Carbon Support



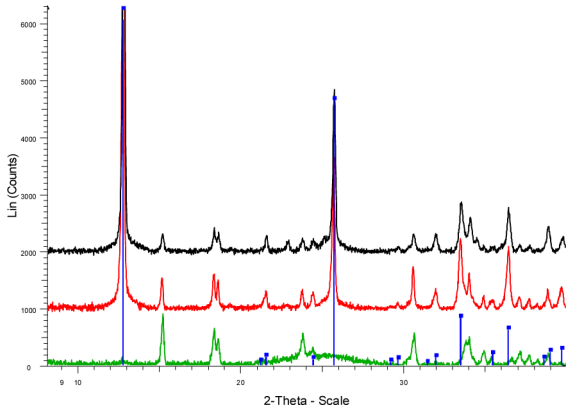


Figure 2. XRD patterns showing the results of the higher copper loading, 2× (Green), 5× (Red), and 10× (Black). Blue ticks correspond to Gerhardite.

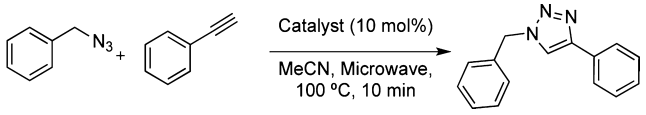
As expected, the different copper loadings did not show much variation on the quantity of the impurity that formed. However, the reaction using the 2× loading was carried out at a lower final temperature and did not result in the formation of Gerhardite: the impurity phase was the only copper material present. The lack of Gerhardite proved to be an advantage, giving a clearer XRD pattern of the impurity, which allowed a better library search of that material. A perfect match was made with the mineral Libethenite ($Cu_2(PO_4)OH$), a phosphorus-containing species, which explains why the copper loading did not affect the quantity of the impurity formed. A sample of Libethenite was then prepared independently from the support material for XRD analysis[19] and gave an even clearer match to the impurities present in the Darco-KB copper-in-charcoal support materials.

We believe Libethenite is formed due to the nature of the carbon support; that is, Darco-KB is formed through the chemical activation of wood using the phosphoric acid process.[20] The residual phosphate on the carbon could interact with the copper nitrate during the reaction to prepare the copper-in-charcoal support material. Libethenite is not observed using Norit A SUPRA as this carbon material is a steam-activated carbon of natural origin.[21]

In order to delineate the role of Libethenite and Gerhardite in the catalytic processes reported by Lipshutz for "Cu/C", we tested our copper containing materials in the CuAAC reaction (Table 1). Treatment of phenyl acetylene and benzyl azide under microwave conditions employing a 10 mol % catalyst loading generally afforded good to excellent yields of a single regioisomer of the triazole.[22] Gerhardite, without the charcoal support (entry 5), performed equally as well as "Cu/C" and was reduced to copper(I) to produced the required polymeric copper(I) acetylide precatalyst, which was easily removed at the end of the reaction by filtration.[23] Under the conditions reported in Table 1, Et_3N was not required for the reactions to proceed, as noted by Lipshutz for "Cu/C".[6a,24] Importantly,

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Table 1. Triazole Formation Using Gerhardite and Lebethenite Supported and Unsupported Materials[a]



entry	material (10 mol %)	yield (%)[b]
1	"Cu/C"	99[c]
2	commercial "Cu/C"	54[d]
3	prepared "Cu/C"	85
4	Gerhardite on NoritA SUPRA	82
5	Gerhardite	89 (97)[e]
6	Libethenite	<5
7	control	<5[f]

[a]General reaction conditions: catalyst (10 mol %), benzyl azide (1.7 mmol), phenyl acetylene (2.6 mmol), MeCN, microwave at 100 °C, 10 min. [b]Isolated yield after column chromatography. [c]Yield reported in ref 6a when using dioxane as solvent and Et_3N (1.1 equiv). [d]Commercial material, see ref 14 for details. [e]Reaction carried out using dioxane as solvent. [f]Reaction carried out in the absence of any catalysts.

Libethenite was found to be inactive in the CuAAC reaction (entry 6). For reasons which are unclear at present, the commercial "Cu/C" performed poorly in this reaction, perhaps due to degradation of the catalyst, although XRD analysis did show good correlation between commercial and our prepared material.[25]

Having noted previously that materials such as $Cu_2(OH)_3OAc$ react with alkynes to initially form copper(I) acetylides,[11d] we were interested in examining the supported materials after the CuAAC reaction. While there was some conversion shown from Gerhardite to copper(I) phenylacetylide during the reaction, it was not a full conversion so a series of time controlled reactions were performed to try to drive the conversion of Gerhardite to copper(I) phenylacetylide.[26] Using the conditions shown in Table 1 the triazole click reaction was catalyzed using a mixture of Gerhardite and Libethenite without the solid support material present. We believed that this would help to remove some of the background noise from the XRD patterns making interpretation easier. The results are shown in Figure 3. The XRD patterns from 0 h to 10 days show the gradual formation of the copper(I) phenylacetylide and the corresponding gradual disappearance of Gerhardite as it is consumed. The Libethenite remains present in all XRD patterns, which shows that it takes no part in the formation of the copper(I) species and hence cannot take part in catalysis of triazole formation.

These observations led us to question why we did not observe CuO or Cu_2O, as had been previously assumed[6] and reported independently by Mehandjiev, Liu, and Wey.[9] The detailed procedures used by the research groups reveal a crucial difference: in the Mehandjiev, Liu, and Wey reports, the final step in the experimental procedure involved the copper-in-charcoal material being calcined at either 503 K,[10a] 523 K,[10b] or >700 K[10c] before the material was analyzed by X-ray powder diffraction. Under the Lipshutz conditions, that final step was not carried out, and as a result, the inorganic salts were not decomposed but remained in the form of Gerhardite and Libethenite.

In summary, we have shown that the procedure[6] used to prepare copper-in-charcoal does not afford CuO or Cu_2O bound to the charcoal matrix as previously assumed. However, Gerhardite is easily prepared and can be stored for long periods without decomposition, as also can, for example, the copper(I) acetylide polymer precatalysts. Hence, the copper species using Cu/C, that is responsible for reactions such as the CuAAC process, has been identified as Gerhardite ($Cu_2(OH)_3NO_3$), which acts as a precatalyst and is reduced under the reaction conditions to a copper(I) acetylide in order to carry out the triazole forming step. Additionally, we observed an impurity phase in the materials prepared using the Darco-KB activated carbon. This impurity was identified as Libethenite, $Cu_2(PO_4)$-OH, and was shown to be inactive in the CuAAC reaction. We are currently investigating the application of Gerhardite to other catalyed processes and early indications show that both Gerhardite and Libethenite can catalyze Ullmann aryl ether synthesis. A full investigation will be published in due course. We anticipate that understanding of the catalyst involved in this heterogeneous system will inspire further studies and advancements in this area.

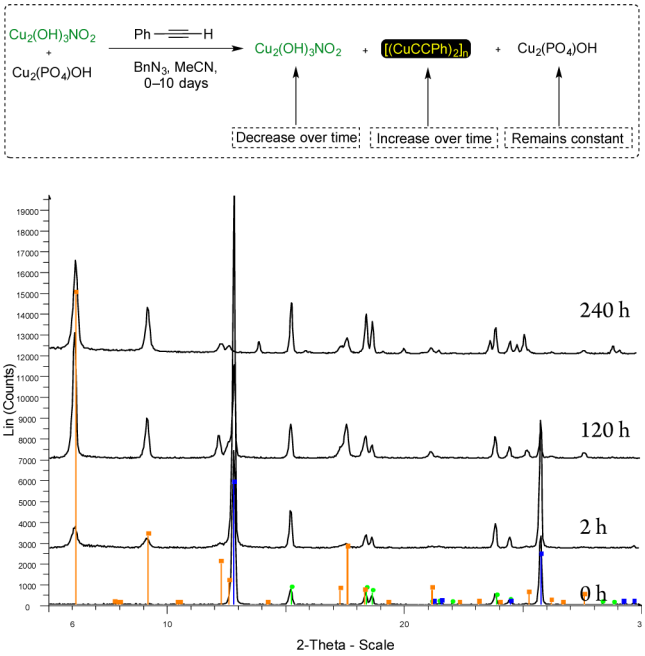


Figure 3. XRD results from the series of time controlled click reactions,[26] showing the formation of copper(I) phenylacetylide (orange) from Gerhardite (blue) not Libethenite (green).

■ ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs501826s.

Experimental procedures, additional XRD data, and additional experiments (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: b.r.buckley@lboro.ac.uk.

Notes

The authors declare no competing financial interest.

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(18) Copper in charcoal, 3 wt %, SKU number 709107, Sigma-Aldrich.
(19) The X-ray powder diffraction pattern obtained from this reaction can be found in the Supporting Information.
(20) See product information page: http://www.norit.com/products-and-services/products/darco-kb-g/.
(21) See product information page: http://www.norit.com/products-and-services/products/norit-a-supra-eur/.
(22) See Table S1 in the Supporting Information for other examples employing Gerhardite as precatalyst in the CuAAC reaction.
(23) The solid material obtained was isolated as a mixture of Gerhardite and the copper(I) acetylide.
(24) See Table S1, entry 2 for a direct comparison of reactivity between "Cu/C" (reported in ref 6a) and Gerhardite.
(25) One could also speculate that this commercial material may have a lower copper loading than the prepared material.
(26) Details of the reactions carried out can be found in the Supporting Information.

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