CHEMCATCHEM
FULL PAPERS

ChemPubSoc Europe

DOI: 10.1002/cctc.201200569

Aerobic Oxidation of Thiols Catalyzed by Copper Nanoparticles Supported on Diamond Nanoparticles

Amarajothi Dhakshinamoorthy, Sergio Navalon, David Sempere, Mercedes Alvaro, and Hermenegildo Garcia*[a]

After purification by Fenton treatment, commercial diamond nanoparticles (NPs) are a suitable solid support for the deposition of Cu nanoparticles. Heating at 500 °C under hydrogen proved to be a convenient annealing process for Fenton-purified diamond NPs that decreased the population of surface carboxylic acid groups and lead to samples with average Cu particle sizes of 3–4 nm. The samples of Cu NPs supported on diamond NPs have been characterized by IR and X-ray photoelectron spectroscopy, as well as XRD and TEM. It was concluded that the samples contained Cu^0 as well as Cu^I and Cu^{II} species. The resulting diamond-supported Cu NPs were highly active for the selective aerobic oxidation of aromatic thiols to the corresponding disulfides, whereas aliphatic thiols exhibited much lower reactivity because of some poisoning and catalyst deactivation produced by aliphatic thiols. The Cu catalysts used for thiophenol oxidation could be reused in four consecutive runs with 4 % of decrease in the catalytic activity. This Cu catalyst exhibited similar catalytic activity, but is considerably more affordable, as an analogous diamond-supported Au catalyst.

Introduction

Disulfides have been extensively used in chemistry[1] and biological studies.[2–4] In biological systems disulfides prevent oxidative damage.[5] Disulfides are also used as reagents for organic syntheses to sulfenylate various anions[6] and as a protecting group for thiols.[7] In industry, disulfides are commonly used to vulcanize rubber and elastomers.[4]

Oxidative coupling of thiols is the most common method for disulfide synthesis. Reagents that have been used to perform the S–S oxidative coupling include permanganate,[8] halogens,[9] iron(III) chloride,[10] organometallic complexes,[11,12] and peroxides.[13] Transition metal complexes have also been used as catalysts for the conversion of thiols to disulfides.[14–16] One of the main problems associated with these methods is the need of stoichiometric reagents, long reaction times and high catalyst loading as well as undesirable side products arising from over-oxidation of disulfides. Further, tedious workup procedure has to be implemented to isolate the desired products from the oxidizing reagents. For this reason, aerobic catalytic oxidation of thiols to disulfides is a good alternative to those using other oxidizing reagents. The aerobic oxidation of thiols to disulfides has been reported with heterogeneous catalysts like metal-organic frameworks,[17] graphite oxide[18] and gold supported on CeO_2.[19]

Herein, we report the preparation of copper nanoparticles (NPs) supported on diamond NPs and their catalytic activity for the aerobic oxidation of thiophenols to their corresponding diphenyldisulfide. The main advantages of this method are low catalyst loading, short reaction time, cost effectiveness of the catalyst and high product selectivity. In recent precedent, we have shown that the inertness of diamond NP surface makes this carbonaceous material suitable as support of active metal NPs in oxidation reactions.[20]

Results and Discussion

Characterization of Cu/D and Cu/DH

BET surface area of the commercial diamond NPs was $250\,m^2g^{-1}$, whereas the areas of the Fenton-treated diamond NPs (D) and hydrogen-annealed supports (DH) slightly increased to 282 and $296\,m^2g^{-1}$, respectively. This increase was attributed to the removal of amorphous soot matter present in the commercial diamond samples.[20]

FTIR spectra of the commercial, Fenton-treated, and annealed diamond NPs with or without Cu deposition are presented in Figure 1. As previously reported,[20] commercial diamond functionalization is needed to introduce surface hydroxyl groups that will further interact with the metal NPs.[20,24] The sample D presented a broad band from 3674 to $2832\,cm^{-1}$ corresponding to –OH groups of alcohol and acid carboxylic functionalities. In addition, the presence of carboxylic groups is revealed by the C=O band appearing around $1754\,cm^{-1}$. Also, a characteristic band at $1132\,cm^{-1}$ corresponding to the C–O bond is observed.

---

[a] Dr. A. Dhakshinamoorthy, Dr. S. Navalon, D. Sempere, Dr. M. Alvaro, Prof. Dr. H. Garcia
Instituto Universitario de Tecnología Química CSIC- UPV and
Departamento de Química, Univ. Politécnica de Valencia
Av. De los Naranjos s/n, 46022 Valencia (Spain)
Fax: (+34) 9638-7807
E-mail: hgarcia@qim.upv.es

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201200569.

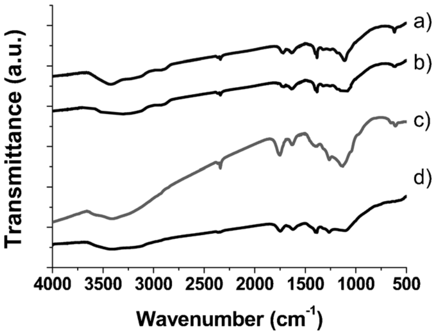


Figure 1. FTIR spectra of diamond NP samples. a) DH, b) DH with Cu deposited (Cu/DH), c) D, and d) D with Cu deposited (Cu/D).

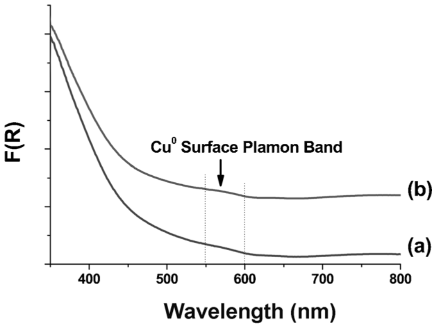


Figure 3. Diffuse reflectance spectra (plotted as the Kubelka–Munk function of the reflectance, R) of the catalysts a) Cu/D and b) Cu/DH.

Further, annealing treatment at 500 °C under H_2 atmosphere of the D samples produced a more symmetric band from 3674 to 3000 cm^{-1} (indicating the prevalence of alcohol OH groups), together with a clear decrease of the carbonyl band intensity and shifting to 1726 cm^{-1}. Also, a more symmetric and less intense C–O band at 1132 cm^{-1} is observed. In addition, DH sample presents the vibration corresponding to C–H vibrations 2917 and 1384 cm^{-1}. These facts indicate that thermal treatment under H_2 produces the reduction of some carboxylic functionalities to alcohol groups or even further to aliphatic carbons, decreasing the density of surface carboxylic acid groups. After Cu deposition, the –OH vibration band in both Cu/D and Cu/DH samples diminished indicating the interaction of the copper species with hydroxyl groups as reported previously for the case of gold supported on D.[20]

TEM analysis reveals an influence of the copper particle size depending on the support, namely D or DH. Figure 2 shows representative TEM images and particle size distribution of Cu/D and Cu/DH (see the Supporting information, Figure S1). As it can be seen, Cu/D presents a broad particle size distribution up to 19 nm with the main population centered at 6–7 nm. On the other hand, Cu/DH samples show a narrower particle size distribution centered at 3–4 nm with a maximum size of 10 nm. These data reveal the benefits of copper NP deposition on thermally H_2-annealed DH sample with a lower population of carboxylic acid groups. Particle sizes similar to those of Cu/DH were obtained for Au/DH. In particular, Au/DH presented a particle size distribution centered at 5–6 nm with a maximum particle size of 10 nm (Figure S2).

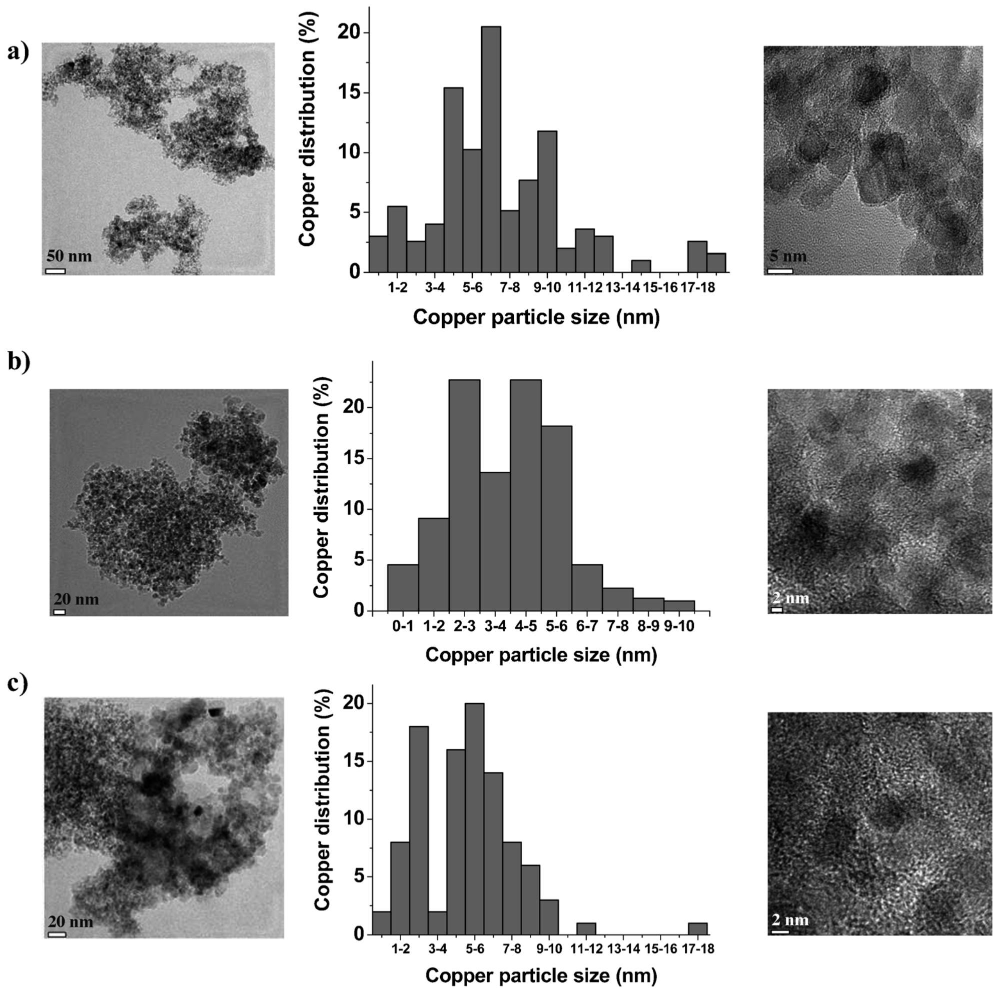


Figure 2. TEM images and particle size distributions of a) Cu/D, b) Cu/DH, and c) Cu/DH after reuse.

Shown in Figure 3 are the diffuse reflectance spectra for the different copper catalysts. As it can be seen there, the band at 550–600 nm corresponds to the surface plasmon band of metallic Cu NPs[25] that we propose to correspond to the small metal Cu NPs as revealed by TEM.[26] Further, the absorption band at approximately 640 nm and a more intense band above 700 nm could indicate the presence of a residual population of Cu^{2+} ions.[25] Notably, although the polyol preparation method would reduce Cu^{2+} ions to Cu^0, the metallic copper can still undergo partial oxidation under atmospheric conditions.

The X-ray diffractograms of Cu/D and Cu/DH catalysts showed the presence of a low-intensity peak at $2\theta = 50.8°$ corresponding to Cu NPs (Figure 4) in accordance with the good dispersion observed in the TEM measurements (Figure 2 and Figure S1). Other diffraction peaks of metallic Cu NPs at $2\theta =$ 43.6 and 74.4° corresponding to the Cu (111) and Cu (202) facets, respectively,[26] should be masked by the diffraction pattern of diamond NPs centered at approximately 43.6 and 74.8°. In addition, the presence of a weak diffraction peak at $2\theta = 65°$ attributable to Cu_2O was also observed.

The presence of oxidized Cu^{II} on the surface of the catalyst was determined by X-ray photoelectron spectroscopy (XPS, Figure 5). Typical Cu^0 and Cu^I peaks are indistinguishable here because they are separated by only 0.1 eV; therefore, we attributed the deconvoluted peak at 932.4 eV to a combination of these reduced copper species.[27,28] In contrast, the binding energy of Cu^{II} can be easily distinguished from the energies of Cu^0 and Cu^I and, thus, the peak at approximately 934.0 eV was assigned to oxidized Cu^{II} species.[28] It is known that Cu NPs easily undergo oxidation, at least near the surface, under aerobic conditions.

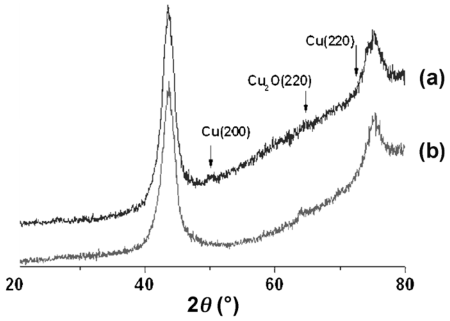


Figure 4. X-ray diffractograms of the catalysts a) Cu/D and b) Cu/DH.

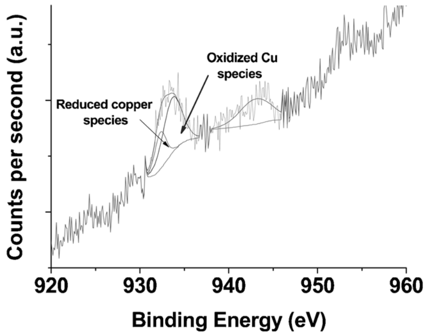


Figure 5. X-ray photoelectron spectra of Cu $2p_{3/2}$ line measured for the Cu/DH sample. The plot also shows the best deconvolution of the experimental peaks.

These data show that Cu NPs interact mainly with the –OH groups of D and DH supports, the thermal annealing under H_2 leading to Cu NPs with sizes centered at 3–4 nm that are smaller than the sizes of the unannealed D NPs at approximately 6–7 nm. In addition, the presence of metallic and oxidized copper species has been confirmed by XPS measurements.

Catalytic activity of Cu/DH

Thiophenol (**1**) was selected as a model substrate to optimize the reaction conditions. Aerobic oxidation of **1** to diphenyldisulfide (**2**) in the absence of a catalyst resulted in 7% conversion. The aerobic oxidation of **1** to **2** is promoted by the Cu catalysts. Thus, the use of Cu/D resulted in 60% conversion of **1** to **2** in 4 h. Using Cu/DH as a catalyst, quantitative conversion of **1** was achieved in 4 h in the presence of oxygen with a selectivity of **2** of >99% (Figure 6). The better catalytic performance of Cu/DH over Cu/D is in agreement with the general trend of the beneficial influence of small particle size on the catalytic activity and indicates the advantages of H_2 annealing reducing the population of surface carboxylic groups before deposition Cu NPs on diamond. Thus, the following experiments were all conducted with this Cu/DH catalyst.

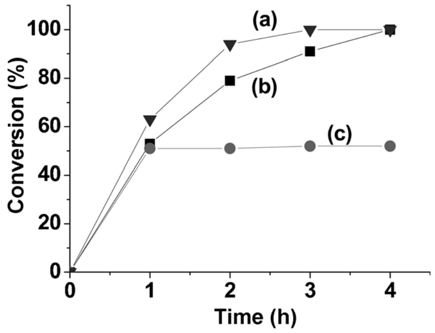


Figure 6. Time–conversion plot for the aerobic oxidation of **1** to **2** using Au/DH and b) Cu/DH catalysts. c) Hot-filtration test under the same experimental conditions with Cu/DH as the catalyst. For reaction conditions, see Table 1, entry 3.

Replacing oxygen by nitrogen led to incomplete oxidation of **1** that is probably promoted by residual oxygen still present in the system. Typically, oxidation of **1** with Cu/DH was performed at a molar ratio **1**/Cu of 666, achieving complete conversion in 4 h. Doubling the amount of **1** from 1 mmol to 2 mmol also resulted in complete conversion in 4 h under the same experimental conditions. Thus, we were interested in probing the catalyst stability in the presence of large excess of **1** (10 mmol). Under these conditions the catalyst lost its activity after reaching 90% conversion (Figure S3). In this case with a large excess of substrate (molar ratio **1**/Cu of 5772), the turnover number and the turnover frequency was approximately 5700 cycles and 825 h^{-1}, respectively. We attribute catalyst deactivation to the oxidation of metallic Cu^0 or Cu^I to Cu^{II} and to the poisoning effect of sulfur-containing products or to a combination of both.

In addition, aerobic oxidation of **1** to **2** in the presence of Cu/DH with 2,2′,6,6′-tetramethylpiperidine *N*-oxide (TEMPO) and 2,6-di-*tert*-butylhydroxytoluene as co-catalysts resulted in high conversion of **1**, which agrees with the role of TEMPO as a co-catalyst in some copper catalysts promoting benzyl alcohol oxidation and with the absence of free-radical oxidation.[29] Hence, herein TEMPO rather acts as a cocatalyst trapping the radicals formed during the course of the reaction.

To gain understanding on the role of diamond as support, copper NPs were also supported on activated carbon (AC) and graphite (G) and their catalytic activity tested in the aerobic oxidation of **1**. The initial reaction rates and final conversion of **1** with these catalysts were lower than those achieved with Cu/DH as a catalyst (Table 1 and Figure S4). These experimental results show the advantage of an inert diamond surface over other types of carbons.

Table 1. Aerobic oxidation of **1** to **2** using different catalysts.[a]

Run	Catalyst	t [h]	Conv. [%][b]	Selectivity [%][b]
1		4	7	98
2	Cu/D	4	60	99
3	Cu/DH	4	100	99
4	Cu/DH 1st reuse	4	99	99
5	Cu/DH 2nd reuse	4	97	99
6	Cu/DH 3rd reuse	4	96	99
7	Cu/DH	1	89[c]	99
8	Cu/DH	4	100[c]	99
9	Cu/DH	1	13[d]	98
10	Cu/DH	24	92[d]	99
11	Cu/DH	2	96[e]	98
12	Cu/DH	4	99[f]	98
13	Cu/AC	1	16	98
14	Cu/AC	4	34	98
15	Cu/G	1	43	99
16	Cu/G	4	78	99
13	Au/DH	3	100	99

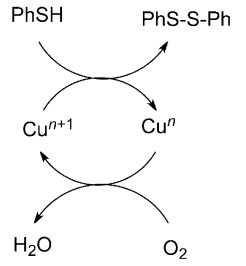
[a] Reaction conditions: Thiophenol (1 mmol), catalyst (20 mg, 0.5 wt.%), ethanol (4 mL), oxygen purged through balloon, 70 °C. [b] Determined by GC. [c] Thiophenol (2 mmol), catalyst (40 mg, 0.5 wt.%), ethanol (8 mL), oxygen purged through balloon, 70 °C. [d] Thiophenol (10 mmol), catalyst (20 mg), ethanol (10 mL), oxygen purged through balloon, 70 °C. [e] With TEMPO. [f] With 2,6-di-*tert*-butylhydroxytoluene.

Finally, Au/DH was used as a catalyst for the aerobic oxidation of **1** to **2**, and its activity was compared with that of Cu/DH (Figure 6). Although the initial reaction rate and the final conversion were somewhat higher for Au/DH than for Cu/DH, both metals exhibited high activity in this oxidation experiment. The higher activity of Au is not totally unexpected with regard to the strong interaction of thiols with gold and the high oxidation activity of Au catalysts.[19] However, considering the cost and availability, the development of such Cu catalysts would be more competitive than that of analogous catalysts based on precious metals.

Heterogeneity of the reaction and absence of Cu leaching was addressed by a hot-filtration test. After achieving about 51 % conversion of **1**, Cu/DH catalyst was removed from the reaction mixture by hot filtration and the resultant reaction mixture was allowed to react further in the absence of solid (Figure 6). As conversion did not increase after removal of Cu/DH, the possibility that oxidation was promoted by any soluble Cu species was ruled out.

Reusability of Cu/DH for the aerobic oxidation of **1** to **2** was studied by performing four consecutive runs with Cu/DH catalyst. A 4 % conversion decrease was observed (entries 4–6, Table 1). Furthermore, inductively-coupled plasma mass spectrometry analysis after the reuse experiments revealed that copper leaching after the first use was about 2.1 % of the initial Cu content of the Cu/DH catalyst, whereas in the subsequent reuse experiments negligible Cu leaching was observed. In addition, TEM analysis of the reused sample (see Figure 2) revealed a slight Cu NP size increase to an average of 5–6 nm, although large Cu NPs of 17 nm diameter, which were not present in the fresh catalyst sample, were also observed.

Based on these results, we propose that the reaction of **1** with Cu/DH takes place through the intermediacy of surface-bound thiyl radicals that undergo self-coupling to give **2**. Upon the generation of each thiyl radical, partially oxidized copper species is reduced by **1**, as shown in Scheme 1.



Scheme 1. Proposed mechanism for aerobic oxidation of **1** to **2** catalyzed by Cu/DH.

The scope of this catalyst was further studied by using different aromatic and aliphatic thiols under the optimized conditions (Table 2). 4-Fluoro-, 4-chloro-, 4-methyl-, 4-methoxy-, and 2-aminothiophenol showed 99 % conversion with more than 99 % selectivity to the corresponding disulfide. On the other hand, 2-mer-

Table 2. Aerobic oxidation of thiols to disulfides catalyzed by Cu/DH.[a]

$$\mathrm{RSH} \xrightarrow[\mathrm{C_2H_5OH,\ 70^oC}]{\mathrm{Cu/DH}} \mathrm{RS\text{-}SR}$$

Run	Thiol	t [h]	Conv. [%][b]	Selectivity [%][b]
1	thiophenol	4	>99	99
2	4-fluorothiophenol	2	>99	99
3	4-chlorothiophenol	2	>99	99
4	4-methylthiophenol	2.5	>99	99
5	4-methoxythiophenol	2	>99	98
6	2-aminothiophenol	1.5	>99	98
7	2-mercaptopyridine	3	57	98
8	1-napthylthiol	8	5	96
9	thiobenzoic acid	24	–	–
10	1-hexanethiol	29	17	98
11	cyclohexyl mercaptan	29	12	98
12	benzyl mercaptan	29	35	98
13	3-chloro-1-propanethiol	24	44	98

[a] Reaction conditions: Thiol (1 mmol), catalyst (20 mg), ethanol (4 mL), oxygen purged through balloon, 70 °C. [b] Determined by GC.

captopyridine showed 57% conversion in 3 h, attributable to the competing coordination of oxidizing copper sites with the N atom of the pyridine ring. 1-Napthylthiol showed very poor reactivity because of the low solubility of this substrate in ethanol. Further, thiobenzoic acid showed no reactivity. Aliphatic thiols were less reactive than aromatic thiols. For example, 1-hexanethiol showed 17% conversion in 29 h. Cyclohexyl mercaptan and benzyl mercaptan showed 12 and 35% conversion, respectively, in 29 h. Finally, 3-chloro-1-propanethiol showed 44% conversion in 24 h. To compare the activity of Cu/D, Au/D was used as a catalyst under the same conditions and exhibited a reactivity similar to that of Cu/D (Figure 7).

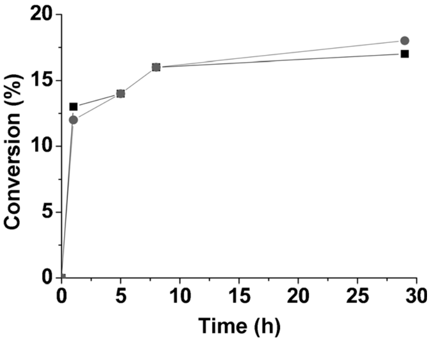


Figure 7. Aerobic oxidation of 1-hexanethiol using Au/DH (●) and Cu/DH (■) as catalysts.

To understand the reasons of the lower catalytic activity of Cu/DH for aliphatic thiols compared to that for thiophenols, the coupling reaction of cyclohexanethiol to dicyclohexyldisulfide was performed for prolonged time to ensure the maximum yield. A conversion of 12% was achieved after 29 h. At this time an extra amount of fresh Cu/DH catalyst was added, whereby the conversion increased to 27%. This suggests that the limitation in the product yield of aliphatic thiols is not based on thermodynamics but owing to catalyst deactivation. Probably the strong adsorption of aliphatic disulfides or other sulfur-containing byproducts on the copper reaction sites was causing their deactivation. For this reason the addition of fresh catalyst could increase the product yield. Similarly, the strong adsorption of thiobenzoic acid on the copper sites would be responsible of the failure of Cu/DH to promote the oxidation of this compound, whereas the other aromatic thiols tested were easily oxidized.

Conclusions

Fenton-treated diamond nanoparticles (NPs) have been found to be suitable solid supports for copper NPs that catalyze the selective aerobic oxidation of aromatic thiols to disulfides. Although analogous diamond-supported gold catalysts exhibited a somewhat higher activity in this reaction, copper is a more economical metal. Hydrogen annealing improved the performance of the diamond support by decreasing the population of carboxylic groups, thus leading to smaller Cu NPs that exhibit higher catalytic activity. Upon reuse, the catalyst experienced a slight deactivation that has been attributed to a minor Cu leaching and an increasing of the average Cu NP size. In the case of aliphatic thiols, the Cu/DH catalyst became deactivated before high conversions were reached.

Experimental Section

Hydrogen peroxide solution in water (30%, v/v), nitric acid (65%), hydrochloric acid (37%, ACS reagent), sulfuric acid (98%), $HAuCl_4\cdot3H_2O$, $Cu(NO_3)_2\cdot2H_2O$, NaOH (ACS reagent) and diamond nanopowder (ref: 636444, 95%) were commercial samples from Sigma–Aldrich. Milli-Q water was used in all the experiments. The other reagents used were of analytical or HPLC grade. Other starting materials were obtained commercially from Aldrich and used without any further purification unless otherwise noted.

Fenton treatment of commercial diamond NPs was performed by suspending raw diamond nanopowder (0.5 g) in 150 mL H_2O_2 (30%, v/v) in a 500 mL open flask. The pH was adjusted at 3 using HNO_3 (0.1 M) and maintained at this value during all the process. This slurry was sonicated in an ice-refrigerated ultrasound bath and held at 1–5 °C for 20 min. Then, a freshly prepared aqueous solution of $Fe(SO_4)\cdot7H_2O$ (mg mL^{-1}) at pH 3 was slowly dropped for 1 h while observing intense gases evolution. (caution: the Fenton reaction is a highly exothermic reaction and occurs with evolution of heat and gases. The process must be carried out with care in a well-ventilated fume hood whilst wearing goggles and appropriate personal safety items). After 1 h, additional amounts of $H_2O_2\cdot$(50 mL) and $Fe(SO_4)\cdot7H_2O$ were added until complete H_2O_2 decomposition as evidenced by titration with titanyl oxalate.

After the Fenton treatment, the suspension was diluted with distilled water and allowed to reach RT. Then, several washings were made using an aqueous solution of sulfuric acid (0.1 M) until the absence of iron detected by colorimetric method using KSCN. The excess of acid was removed by performing five consecutive centrifugation–redispersion (14000 rpm) cycles with Milli-Q water. Diamond NPs sediment at the bottom of the centrifuge tube under these conditions and can be easily recovered and re-suspended. The pH value of the supernatant at the fifth centrifugation–redispersion cycle was neutral. Finally, the Fenton-treated diamond NPs were submitted to overnight freeze-drying to give dry, purified diamond NPs (D).

Additionally, D was submitted to a subsequent annealing treatment under continuous H_2 flow. In particular, D powder was placed in a quart reactor under H_2 flow (100 mL min^{-1}) and heated using a ramp of 8 °C min^{-1} until the temperature reached 500 °C and maintained for 6 h. Then, the sample was cooled at RT and the support labeled as DH. This reduction treatment decreases the number of surface defects by increasing the population of –OH groups.[21]

Preparation of Cu/D, Cu/DH, and Au/DH catalysts was accomplished by using the polyol method.[22,23] Briefly, 200 mg of the diamond support (D or DH) were suspended in 80 mL of ethylene glycol and sonicated for 30 min. Then, the corresponding amount of gold or copper salts dissolved in water was added to the diamond suspension to achieve 0.5 wt.% loading. Under vigorous stirring the suspension was heated up to 85 °C and allowed to react for 4 h. After cooling the reaction at RT the powder suspended was recovered by centrifugation at 14000 rpm. Then the supernatant was removed and the catalyst dispersed in ethanol and washed by performing three consecutive centrifugation–redispersion cycles with acetone and subsequently other three with water.

Finally, the catalysts (Cu/D, Cu/DH, and Au/DH) were freeze-dried. The same procedures were followed for the preparation of Cu/AC and Cu/G by replacing D or DH either by AC or G.

By using inductively coupled plasma atomic emission spectroscopy (ICP-AES) chemical analysis, the metal loading (0.5 wt.%) deposited on the functionalized diamond NPs was confirmed. FTIR spectra of the different samples were recorded on a Nicolet 710 FTIR spectrophotometer by using KBr disks of the samples prepared by compression at 10 Ton for 2 min. Diffuse reflectance optical spectra were recorded by using a CARY 5G UV-Vis-NIR spectrophotometer adapted with an integrating sphere. X-ray diffractograms (XRD) were recorded by using a Philips X-Pert diffractometer equipped with a graphite monochromator, operating at 40 kV and 45 mA and employing Ni filtered $Cu_{K\alpha}$ radiation ($\lambda = 0.1542$ nm). TEM and high resolution TEM (HRTEM) of the different samples were obtained by using a TECNAI G2 F20 (FEI) instrument operating at 200 kV with a resolution of 0.24 nm. The particle size distribution was estimated by counting over 300 particles. The percentage conversion, purity, and relative yields of the final products were determined by using a Hewlett Packard 5890 series II gas chromatograph with an FID detector and high-purity helium as the carrier gas. The products were identified by GC-MS by using a Hewlett Packard 6890 series spectrometer.

A 50 mL round-bottomed flask was charged with the catalyst (20 mg) in ethanol (4 mL) and the substrate (1 mmol). This reaction mixture was purged with oxygen through balloon. Then it was stirred for the required time at 70 °C. The reaction was monitored periodically by analyzing the sample with GC until the completion of reaction. The mass balances of the recovered reaction mixture accounted for more than 95% of the initial substrate, as confirmed by GC using nitrobenzene as the external standard. The yields of the product were determined by using nitrobenzene as the external standard considering the response factors unity.

Reuse experiments were performed as given in entry 7, Table 1. After the catalytic oxidation the catalyst was recovered by centrifugation. Then, the catalyst was washed in ethanol, acetone and water three times each solvent, and dried under air at RT. Then the isolated catalyst was treated with ethylene glycol at 85 °C for 5 h followed by different cycles of washing/centrifugation with ethanol and water. The recovered catalyst was used for the next run with appropriate substrate and solvent.

Acknowledgements

Financial support by the Spanish Ministry of Science and Education (Consolider MULTICAT, CTQ-2009-11856) is gratefully acknowledged.

Keywords: aerobic oxidation · copper · diamond · nanoparticles · thiophenol

[1] E. Zysman-Colman, D. N. Harpp, *J. Org. Chem.* **2005**, *70*, 5964.
[2] R. J. Cremlyn in *An Introduction to Organosulfur Chemistry*, Wiley, New York, **1996**.
[3] G. H. Whitham in *Organosulfur Chemistry*, Oxford University Press, Oxford, **1995**.
[4] S. Ghammamy, M. Tajbakhsh, *J. Sulfur Chem.* **2005**, *26*, 145.
[5] H. Karami, M. Montazerozohori, M. H. Habibi, *J. Chem. Res.* **2006**, *8*, 490.
[6] L. Bischoff, C. David, L. Martin, H. Meudal, B.-P. Roques, M.-C. Fournie-Zaluski, *J. Org. Chem.* **1997**, *62*, 4848.
[7] F. Hosseinpoor, H. Golchoubian, *Catal. Lett.* **2006**, *111*, 165.
[8] N. A. Noureldin, M. Caldwell, J. Hendry, D. G. Lee, *Synthesis* **1998**, 1587.
[9] M. H. Ali, M. McDermott, *Tetrahedron Lett.* **2002**, *43*, 6271.
[10] A. R. Ramesha, S. Chandrasekaran, *J. Org. Chem.* **1994**, *59*, 1354.
[11] D. K. Y. Tan, J. W. Kee, W. Y. Fan, *Organometallics* **2010**, *29*, 4459.
[12] K. Y. D. Tan, G. F. Teng, W. Y. Fan, *Organometallics* **2011**, *30*, 4136.
[13] A. R. Hajipour, S. E. Mallakpour, H. Adibi, *J. Org. Chem.* **2002**, *67*, 8666.
[14] H. Golchoubian, F. Hosseinpoor, *Catal. Commun.* **2007**, *8*, 697.
[15] S. M. S. Chauhan, A. Kumar, K. A. Srinivas, *Chem. Commun.* **2003**, 2348.
[16] K. Tanaka, K. Ajiki, *Tetrahedron Lett.* **2004**, *45*, 25.
[17] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, *Chem. Commun.* **2010**, *46*, 6476.
[18] D. R. Dreyer, H.-P. Jia, A. D. Todd, J. Geng, C. W. Bielawski, *Org. Biomol. Chem.* **2011**, *9*, 7292.
[19] A. Corma, T. Rodenas, M. J. Sabater, *Chem. Sci.* **2012**, *3*, 398.
[20] S. Navalon, R. Martin, M. Alvaro, H. Garcia, *Angew. Chem.* **2010**, *122*, 8581; *Angew. Chem. Int. Ed.* **2010**, *49*, 8403.
[21] S. Osswald, G. Yushin, V. Mochalin, S. Kucheyev, Y. Gogotsi, *J. Am. Chem. Soc.* **2006**, *128*, 11635.
[22] K. J. Carroll, J. U. Reveles, M. D. Shultz, S. N. Khanna, E. E. Carpenter, *J. Phys. Chem. C* **2011**, *115*, 2656.
[23] R. J. Joseyphus, K. Shinoda, D. Kodama, B. Jeyadevan, *Mater. Chem. Phys.* **2010**, *123*, 487.
[24] R. Martin, S. Navalon, J. J. Delgado, J. J. Calvino, M. Alvaro, H. Garcia, *Chem. Eur. J.* **2011**, *17*, 9494–9502.
[25] C. M. Chanquía, L. Andrini, J. D. Fernández, M. E. Crivello, F. G. Requejo, E. R. Herrero, G. A. Eimer, *J. Phys. Chem. C* **2010**, *114*, 12221.
[26] H. Lei, Y. Tang, J. Li, J. Luo, *Appl. Phys. Lett.* **2007**, *91*, 113.
[27] K. Yoshida, C. Gonzalez-Arellano, R. Luque, P. L. Gai, *Appl. Catal. A* **2010**, *379*, 38.
[28] T.-Y. Dong, H. H. Wua, C. Huang, J. M. Song, I. G. Chen, T. H. Kao, *Appl. Surf. Sci.* **2009**, *255*, 3891.
[29] P. Gamez, I. W. C. E. Arends, J. Reedijk, R. A. Sheldon, *Chem. Commun.* **2003**, 2414.

Received: August 20, 2012