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Mild and selective catalytic oxidation of organic substrates by a carbon nanotube-rhodium nanohybrid†

Simon Donck,a Edmond Gravel,a Alex Li,a Praveen Prakash,a Nimesh Shah,b Jocelyne Leroy,c Haiyan Li,d Irishi N. N. Namboothiri*b and Eric Doris*a

A heterogeneous catalyst was assembled by stabilization of rhodium nanoparticles on carbon nanotubes. The nanohybrid was used for the catalytic aerobic oxidation of diverse substrates such as hydroquinones, hydroxylamines, silanes, hydrazines and thiols, at room temperature. The system proved very efficient on the investigated substrates and demonstrated high selectivity.

The selective oxidation of organic compounds under mild conditions is of practical importance in synthetic chemistry. In addition to classical stoichiometric processes, catalytic systems have been devised to perform oxidation reactions.1 Further improvements in terms of sustainability were also achieved by supporting the catalysts, thus allowing their reclaim and reuse.2 Among the various catalyst supports, nanostructured carbon allotropes, in particular carbon nanotubes (CNTs), have emerged as highly promising platforms that provide unique advantages such as chemical, thermal, and mechanical stability in liquid media, inertness, high specific surface area, and chemically tunable topography.3 We previously reported supramolecular assemblies of metallic nanoparticles (e.g. Au, Pd, Ru) on carbon nanotubes. These assemblies afforded metal-coated CNTs that were subsequently used in the heterogeneous catalysis of various organic transformations.4 In the course of our investigations we demonstrated that CNTs acted as synergistic support capable of enhancing the performances of the catalytic metal. With these critical features in mind, we sought to expand the scope of our nanohybrid systems by developing a catalyst that would promote a broad scope of oxidation reactions under mild and sustainable conditions. In the present article, we report the assembly and use of a CNT-supported rhodium catalyst (Fig. 1) for the selective oxidation of various substrates, including hydroquinones, silanes, hydroxylamines, hydrazines, and thiols.

The CNT-rhodium catalyst was assembled using a layer-by-layer approach according to a procedure adapted from our previous work.4b Briefly, carbon nanotubes were first sonicated in the presence of amphiphilic nitrilotriacetic-diyne (DANTA) surfactants in water, leading to the formation of supramolecular structures with a nanoring shape at the surface of the CNTs. While the hydrophobic portion of DANTA supported nanostructured carbon allotropes, in particular carbon nanotubes (CNTs), have emerged as highly promising platforms that provide unique advantages such as chemical, thermal, and mechanical stability in liquid media, inertness, high specific surface area, and chemically tunable topography.3 We previously reported supramolecular assemblies of metallic nanoparticles (e.g. Au, Pd, Ru) on carbon nanotubes. These assemblies afforded metal-coated CNTs that were subsequently used in the heterogeneous catalysis of various organic transformations.4 In the course of our investigations we demonstrated that CNTs acted as synergistic support capable of enhancing the performances of the catalytic metal. With these critical features in mind, we sought to expand the scope of our nanohybrid systems by developing a catalyst that would promote a broad scope of oxidation reactions under mild and sustainable conditions. In the present article, we report the assembly and use of a CNT-supported rhodium catalyst (Fig. 1) for the selective oxidation of various substrates, including hydroquinones, silanes, hydroxylamines, hydrazines, and thiols.

The CNT-rhodium catalyst was assembled using a layer-by-layer approach according to a procedure adapted from our previous work.4b Briefly, carbon nanotubes were first sonicated in the presence of amphiphilic nitrilotriacetic-diyne (DANTA) surfactants in water, leading to the formation of supramolecular structures with a nanoring shape at the surface of the CNTs. While the hydrophobic portion of DANTA absorbed at the surface of the CNTs by van der Waals interactions, its hydrophilic head was oriented outward, at the interface with the aqueous medium. The rings were subsequently polymerized by UV irradiation which reinforced the cohesion of the assembly around the CNT. In a second step, a polycationic polymer (PDADMAC) layer was deposited on
the primary coating and rhodium nanoparticles (RhNPs) were added to afford the final nanohybrid (RhCNT). Transmission electron microscopy (TEM) indicated that the RhNPs were of spherical shape, and size evaluation by statistical diameter measurement gave a mean particle diameter of ca. 2 nm (Fig. 2). The metal content of the aqueous RhCNT suspension was determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis which gave a Rh concentration of 5 mM.

With the rhodium-based nanohybrid in hands, we first investigated its potential in the aerobic oxidation of hydroquinones. The treatment of the latter compounds with cerium ammonium nitrate or chromium oxidents is a classical route to produce quinones.5 Recent developments, exploiting milder conditions, have been reported by Kobayashi et al.6 using polymer incarcered noble metal nanoparticles, by the group of Bianco using carbon nanotube-supported silver nanoparticles with hydrogen peroxide,7 and by our group using gold supported on CNTs in alkaline medium.4c

The rhodium-based catalytic system was set by working with 0.25 mol% of the RhCNT hybrid in a mixture of chloroform and water, under air (open flask), and at room temperature. These base-free conditions constitute an interesting improvement over our recently reported system using AuCNT/K2CO3.4c Under these conditions, hydroquinone 1a was fully converted into para-quinone 2a within 5 h (Table 1, entry 1).

One of the advantages of using heterogeneous catalysis is the possibility to recycle the catalyst, thus reducing the cost and environmental impact of the process. To investigate this key feature, five successive oxidations of 1a were performed with the same RhCNT sample which was recovered by centrifugation after each cycle and reused in the next reaction. No significant decrease of the catalytic activity was observed throughout the different oxidation cycles as quinone 2a was produced in nearly constant yields (94–96%, Table S1).†

To explore the scope of the process, several other 1,4-hydroquinones were treated under the above conditions. Among these, electron-rich trimethyl-substituted 1b as well as 1,4-dihydroxynaphthalene 1c were readily converted to the corresponding 1,4-quinones (entries 2 and 3) in 99 and 98% yields, respectively. On the other hand, chlorinated hydroquinone 1d was only partially converted into the corresponding quinone 2d after 5 h‡ (60% yield, entry 4) and electron-deficient acetyl-substituted hydroquinone 1e could not be oxidized, even upon prolonged exposure to the RhCNT catalyst (entry 5). As an example of the oxidation of 1,2-hydroquinones, the transformation of tert-butyl-substituted catechol (1f) into the corresponding ortho-quinone was efficiently carried out, but required 15 h of reaction to afford a satisfactory yield of product (97% yield, entry 6).

It should be noted that the transformation proceeds with low amounts of RhCNT hybrid at room temperature and requires neither base nor added oxidant species. Thanks to these features, the system stands out as one of the most convenient catalysts described so far for the oxidation of hydroquinones.

We next turned our attention to the aerobic oxidation of silanes. The latter are classically converted to silanols using strong oxidizing agents (e.g. osmium tetroxide, permanganate, ozone, peracids, or peroxides)8 but catalytic systems combining water and oxygen have been devised in recent years. Amongst the heterogeneous catalysts for silane oxidation,9 several noble metal-based systems, such as nanoporous gold,9a carbon-supported palladium nanoparticles,9b and AuCNT9d have been reported but, to the best of our knowledge, rhodium-based systems have not been described so far.

Dimethylphenylsilane (3a) was selected as a model substrate but it failed to react under the reaction conditions that were used for the oxidation of hydroquinones. Nevertheless,

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Table 1 Scope of the RhCNT-catalyzed oxidation of hydroquinones

| Entry | Substrate | 1 Product | 2 Yield |
|-------|-----------|-----------|---------|
| 1     | ![Image](image1.png) | 1a         | 2a       | 96%     |
| 2     | ![Image](image2.png) | 1b         | 2b       | 99%     |
| 3     | ![Image](image3.png) | 1c         | 2c       | 98%     |
| 4     | ![Image](image4.png) | 1d         | 2d       | 60%     |
| 5     | ![Image](image5.png) | 1e         | 2e       | NRc     |
| 6d    | ![Image](image6.png) | 1f         | 2f       | 97%     |

* Conditions: 1 (0.2 mmol), RhCNT (0.25 mol%), 100 μL of a 5 mM aqueous suspension, CHCl3/H2O 3:1 (1 mL), room temp., open flask (air), 5 h. bIsolated yields. c No reaction. d After 15 h of reaction.

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† Increasing the reaction time led to some degradation products.
replacing the binary solvent mixture (CHCl₃/water) with THF permitted to afford silanol 4a in 96% yield within 2 h (Table 2, entry 1) upon treatment of 3a with 0.25 mol% of aqueous RhCNT. It is worth mentioning that no disiloxane by-product was detected by gas chromatography coupled to mass spectrometry (GC-MS).

The recyclability of the catalyst for this process was tested over five consecutive cycles (as described above). The conversion remained as efficient throughout the experiment, with yields of 4a ranging from 93 to 96% (Table S2†), with no need to increase the reaction time.

The scope of the RhCNT-catalyzed oxidation was then investigated on a panel of silanes. To validate the high activity of the system, the oxidation of two admittedly challenging substrates (3b and 3c) was undertaken. The oxidation of deactivated triphenylsilane (3b) afforded triphenylsilanol (4b) in excellent yield (entry 2) in contrast to previously reported supported catalyst. The complete oxidation of hindered trisopropylsilane (3c) into silanol 4c was also achieved (entry 3) even though it required more time than other substrates. As another example, diphenylsilane (3d), which contains two Si–H bonds to be oxidized, was quantitatively transformed to the corresponding diphenylsilanediol 4d (entry 4). Finally, benzylidimethyl silane 3e was also selectively converted to its silanol counterpart 4e (entry 5) despite the formation of trace amounts of condensation by-products (<5% of disiloxane).

We then investigated the RhCNT-mediated oxidation of hydroxylamines through which we expected the formation of the corresponding nitroso derivatives. The nanohybrid-catalyzed oxidation of tert-butyl hydroxylamine 5a in CHCl₃/H₂O afforded the nitroso compound 6a in nearly quantitative yield (Table 3, entry 1). The reaction of N-cyclohexyldihydroxylamine 5b also cleanly produced nitrosocyclohexane 6b in 93% yield (entry 2). It is to be noted that no isomerization of nitrosocyclohexane 6b into the corresponding cyclohexanone oxime was detected, despite the fact that tautomerization is classically observed with substrates bearing a Cα-proton.

While the reaction of aliphatic substrates satisfactorily provided access to nitroso compounds in high yields, aromatic hydroxylamines behaved differently. For example, in the case of phenylhydroxylamine 5c, a dimeric product was obtained in the form of an azoxy derivative 6c (entry 3). The mechanism behind the conversion observed in entry 3 may follow an initial path somehow similar to that of aliphatic substrates where the starting phenylhydroxylamine 5c is slowly oxidized into the corresponding nitroso derivative 5c′ (Scheme 1). As 5c′ accumulates, its condensation with unreacted phenylhydroxylamine 5c affords azoxy derivative 6c after elimination of water. The same comments hold true for aromatic substrates bearing either electron-withdrawing or electron-donating substituents such as 4-cyanophenylhydroxylamine 5d (entry 4) and 4-methoxyphenylhydroxylamine 5e (entry 5) which led to the clean formation of the corresponding azoxy dimers 6d (95% yield) and 6e (89% yield), respectively. Recycling of the catalyst using phenylhydroxylamine 5c as substrate showed no significant decrease in yields of 6c (Table S3†).

Finally, the aerobic oxidation of hydrazines into their corresponding azo derivatives and that of thiols into disulfides were explored. The reaction of 1,2-diphenylhydrazine 7a (Table 4, entry 1) cleanly afforded, after 12 h of reaction in CHCl₃/H₂O, 1,2-diphenyldiazene 8a in 92% yield. Similarly, 1-phenyl-2-trityldiazene 7b reacted smoothly to give 1-phenyl-2-trityldiazene 8b in 88% yield (entry 2). However, diphenylmethylen hydrazine 7c did not react under our reaction conditions and remained unaffected (entry 3). On the other hand, thiophenol 7d was converted into the corresponding disulfide 8d within 12 h of reaction and in 96% yield (entry 4). Substituted thiophenol derivatives were also readily oxidized regardless of electronic deficiency (7e, entry 5) or enrichment (7f, entry 6). It is to be noted that the reaction is not operative with aliphatic thiols (e.g.

### Table 2 Scope of the RhCNT-catalyzed oxidation of silanes

| Entry | Substrate | 3 | Product | 4 | Yield |
|-------|-----------|---|---------|---|-------|
| 1     | PhSi(Me)₂H | 3a | PhSi(Me)₂OH | 4a | 96%   |
| 2     | Ph₂SiH     | 3b | Ph₂SiOH  | 4b | 95%   |
| 3     | iPr₂SiH    | 3c | iPr₂SiOH | 4c | 92%   |
| 4     | Ph₂SiH₂    | 3d | Ph₂Si(OH)₂ | 4d | 92%   |
| 5     | BnSi(Me)₂H | 3e | BnSi(Me)₂OH | 4e | 93%   |

* Conditions: 3 (0.2 mmol), RhCNT (0.25 mol%, 100 µL of a 5 mM aqueous suspension), THF (1 mL), room temperature, open flask (air), 2 h. b Isolated yields. c After 12 h of reaction.

### Table 3 Scope of the RhCNT-catalyzed oxidation of hydroxylamines

| Entry | Substrate | 5 | Product | 6 | Yield |
|-------|-----------|---|---------|---|-------|
| 1     | BuO⁻ＮＨＨ⁺ | 5a | BuO⁻NH₂ | 6a | 99%   |
| 2     | CyO⁻ＮＨＨ⁺ | 5b | CyO⁻NH₂ | 6b | 93%   |
| 3     | PhO⁻ＮＨＨ⁺ | 5c | PhO⁻NH₂ | 6c | 93%   |
| 4     | p(CN)C₆H₅NH(OH) | 5d | p(CN)C₆H₅N⁺ | 6d | 95%   |
| 5     | p(MeO)C₆H₅NH(OH) | 5e | p(MeO)C₆H₅N⁺ | 6e | 89%   |

* Conditions: 5 (0.2 mmol), RhCNT (0.25 mol%), 100 µL of a 5 mM aqueous suspension), CHCl₃/H₂O 3:1 (1 mL), room temperature, open flask (air), 12 h. b Isolated yields. c Ar = p(CN)C₆H₅, d Ar = p(MeO)C₆H₅

### Scheme 1 Postulated mechanism for the formation of azoxy compounds.
1-dodecanethiol). Again, recycling of the RhCNT catalyst (with 1,2-diphenylhydrazine 7a) led to no significant decrease in yields (of 8a) over five successive cycles (Table S4†).

Conclusions

The carbon nanotube-rhodium nanohybrid was found to be an efficient catalytic system to perform mild and selective oxidations of various substrates which include hydroquinones, hydroxylamines, silanes, hydrazines, and thiols. The nanohybrid can be readily recycled and it operates under mild conditions as reactions were conducted at room temperature, with low catalytic loading (0.25 mol%). The system proved very efficient on the investigated substrates and demonstrated high selectivity. The results obtained in the context of this study thus compare favorably to previous reports in terms of scope and overall efficiency.

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