

A simple and versatile approach for the fabrication of paper-based nanocatalysts: low cost, easy handling and catalyst recovery

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A versatile method for the preparation of efficient and reusable nanocatalysts involving the painting of a commercial filter paper with a Pd@CNT ink is here described. The resulting paper-based material provided excellent results in the semi-hydrogenation of alkynes and alkynols and could be recycled at least 5 times without loss of activity nor selectivity. <https://doi.org/10.1002/cctc.201600666>

The development of sustainable processes with minimal environmental impact has been recognized as one of the major challenges of this century.^[1] In this context, heterogeneous catalysis appears as a key tool to achieve the suitable utilization of resources and to preserve and rehabilitate our environment.^[2] Moreover, the application of metal nanoparticles (NPs) as catalysts is of particular interest to maximize the available metal surface area and consequently enhance the catalyst productivity.

Nanocatalysts are usually immobilised on oxides such as silica or alumina, on polymers or on carbon materials.^[3] However, the immobilization of selective catalysts onto cheap and easy handling solid supports is still of general interest and recently, alternative carriers such as textile, paper and cotton have demonstrated to be very attractive.^[4] For instance, the covalent immobilization of chiral organocatalysts on nylon was reported with excellent stability, reactivity and recyclability together with flexibility and cost-efficiency of the support.^[4b] This organotextile was used in several reactions such as acylation of phenol to ester and desymmetrization of anhydrides with very good enantioselectivity. More recently, Nagashima and co-workers reported polycationic salts stabilised palladium nanoparticles immobilized on both cotton and paper as a reusable catalyst for sequential cross-coupling and hydrogenation reactions.^[4c] Conventional filter paper is of inherent interest as catalyst support since it is cost-effective, biodegradable, accessible and flexible. It therefore simplifies the handling of the catalyst, e.g. by manipulation with tweezers, as well as the recycling process. Oleylamine-capped Pd nanoparticles were also absorbed on

paper providing reusable catalysts for Suzuki cross-coupling and nitro-to-amine reduction.^[4d] These results showed that such supports can be efficient although in these examples, the synthetic strategy is complex (covalent grafting of the catalyst)⁴ or limited to a type of NP stabilisers providing interactions with the support.^[4c, 4d] To overcome this latter drawback, the use of an interface between the nanocatalyst and the support appears as a promising approach since it allows the utilization of any type of stabiliser. Carbon nanotubes present a great potential for this role^[5] due to their chemical stability, suitable porous properties and broad functionalization strategies (covalent and non-covalent).^[6] In some cases, their structure also leads to metal-support interaction that can enhance the activity/selectivity of the catalysts.^[7] In addition, multi-walled carbon nanotubes were deposited by chemical vapor deposition on silicon chips followed by decoration with Pd in order to form catalyst support membrane.^[8]

In the present communication, we describe the use of carbon nanotubes as an interface between the metal NPs and the support: the palladium nanoparticles are first grown onto the nanotubes (Pd@CNT) and the resulting hybrid material is subsequently anchored onto paper by simple painting of a Pd@CNT ink (Figure 1).^[9] This general approach is simple, versatile and easily scalable (by printing process of the ink). The paper-based nanocatalyst was applied in the semi-hydrogenation of alkynes and alkynols, providing excellent catalytic performance and allowing its recycling for at least 5 consecutive runs without loss of either activity or selectivity. The Pd nanoparticles were synthesized via a one-pot methodology by decomposition of Pd₂(dba)₃ under H₂ in the presence of tricyclohexylphosphine (PCy₃) and multi-wall carbon nanotubes (MWCNTs) (Figure 1a).^[10] TEM analysis of the resulting hybrid material (Figure 2a) evidenced the homogeneous deposition of small PdNPs with narrow size distribution (2.4 ± 0.9 nm) onto the surface of the CNTs. Thermogravimetric analysis revealed that these Pd@CNT exhibited a content of palladium of ca. 35 wt% (Figure S1 in the Supporting Information).

Subsequently, the preparation of the paper-based nanocatalyst was carried out manually via the painting a conventional filter paper. First, an ink was prepared by sonicating an aqueous mixture of Pd@CNT and sodium dodecylbenzenesulfonate (SDBS) (Figure 1b). The resulting suspension was then painted onto the paper to afford the paper-based nanocatalyst (Figure 1c).^[9] Figure 2b displays the ESEM/EDX (environmental scanning microscopy/energy-dispersive X-ray spectroscopy) micrograph of the paper where the homogeneous dispersion of Pd (red spots) at the surface of the cellulose fibres is evidenced. Analysis by induced couple plasma (ICP) of paper painted with 3, 7 and 10 layers of the

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Pd@CNT ink revealed Pd contents of 0.15, 0.23 and 0.31 wt%, respectively. It is noteworthy that the amount of Pd could be tuned by varying the number of ink layers. The range of Pd loading in these materials is comparable to the method reported by Nagashima.^[4c]

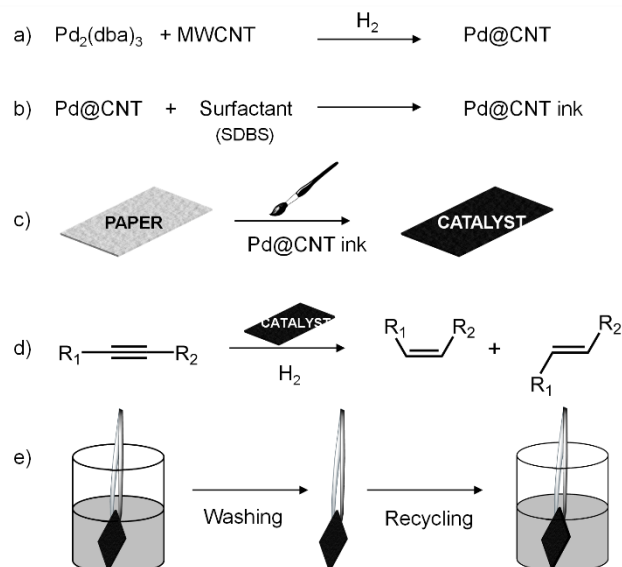


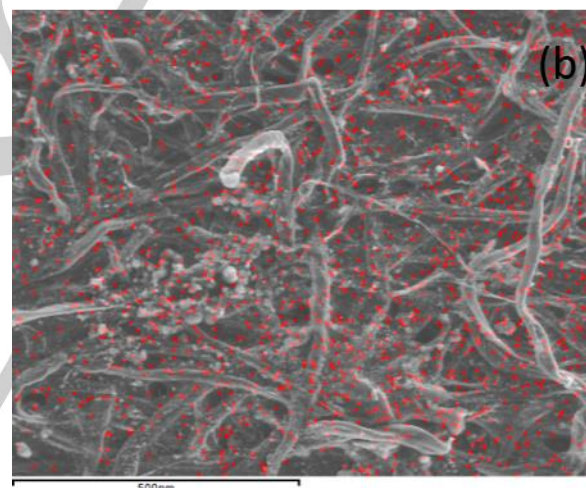
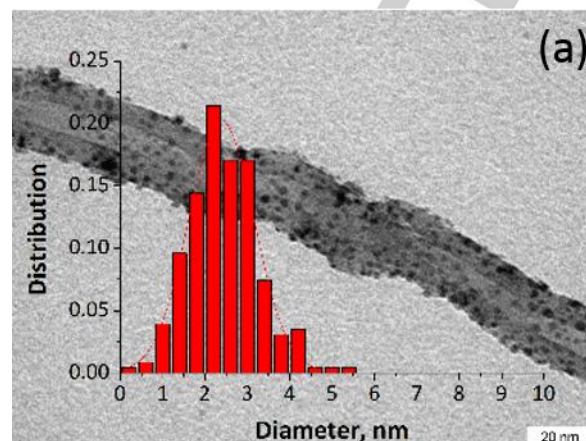
Figure 1. General approach for the preparation of the paper-based nanocatalyst: a) The nanoparticles are grown on the CNTs surface resulting as the Pd@CNT hybrid, b) The hybrid is mixed with surfactants to produce Pd@CNT ink, c) A filter paper is painted with the Pd@CNT, d) The paper catalyst is used for the semi-hydrogenation of the alkynes, 5) The catalyst is washed and recycled for several reactions.

The paper-based catalyst painted with 7 layers was employed in the semi-hydrogenation of alkynes and alkynols which is a process of industrial relevance.^[3] In a typical catalytic experiment, a piece of paper was placed in a tube containing the corresponding substrate in THF. The system was then pressurized with hydrogen (1–10 bar) and heated (30/50 °C) under stirring. After the reaction, the catalytic material was removed using tweezers and the organic phase was analysed by GC-MS.

The experimental conditions (pressure, temperature and time) were initially optimized for a series of terminal and internal alkynes and alkynols (Table S1, S2 and S3).^[11] When necessary, quinoline was used as additive and its concentration was optimized for each substrate.^[12] Excellent selectivity to alkenes at high conversions was achieved for both alkyne and alkynol substrates using this new paper-based catalyst. Milder reaction conditions were required for the partial hydrogenation of terminal alkynes (3 bar H₂, 30 °C) than for that of internal alkynes or alkynols (5 bar H₂, 50 °C).

The promising features of the new paper-based catalyst prompted us to explore the scope of substrates that could be selectively transformed. A series of terminal/internal alkynes and alkynols were therefore tested (Table 1). For alkylic terminal alkynes (Entries 1 and 2), excellent selectivity was obtained for heptyne and octyne at full conversion (89 and 97%, respectively). In addition, conversion, selectivity and composition of the reaction

mixture were plotted as a function of time for 1-heptyne as substrate (Figure S4 SI). When the reactivity of 1, 2 and 4-octyne was compared (Entries 2–4), a decrease in conversion from 100 to 56 % was observed when the triple bond was in an inner position, while the alkene selectivity increased from 89 to 100%.



These results can be related to accessibility issues of the substituted triple bonds, as previously proposed.^[13]

Figure 2. (a) TEM image of Pd@CNT and (b) ESEM image of paper-based nanocatalyst (the red spots correspond to PdNPs deposited onto MWCNTs).

Table 1. Substrate scope of selective hydrogenation of alkynes and alkynols catalysed by the paper-based catalyst.

$R_1-C\equiv C-R_2 \xrightarrow{H_2/Cat} \begin{matrix} R_1 & R_2 \\ \diagdown & / \\ C & =C \\ / & \diagdown \\ R_1 & R_2 \end{matrix} + \begin{matrix} R_1 & R_2 \\ \diagdown & / \\ C & =C \\ / & \diagdown \\ R_1 & R_2 \end{matrix} + \begin{matrix} R_1 & R_2 \\ & \\ C & -C \\ & \\ R_1 & R_2 \end{matrix}$					
			<i>cis</i> -A	<i>trans</i> -A	B
Entry	R1	R2	Conv, %	Sel. A, % (isomer% or sel. <i>cis</i> %)	Sel. B, %
1 ^a	CH ₃ (CH ₂) ₄	H	100	94 (2)	4
2 ^a	CH ₃ (CH ₂) ₅	H	100	89 (4)	7
3 ^a	CH ₃ (CH ₂) ₄	CH ₃	66	95 (98)	1
4 ^a	CH ₃ (CH ₂) ₂	CH ₃ (CH ₂) ₂	56	100 (96)	0
5 ^b	CH ₃ (CH ₂) ₂	CH ₃ (CH ₂) ₂	98	100 (95)	0
6 ^a	Ph	H	62	94	6
7 ^a	Cy	H	87	95	5
8 ^b	Ph	CH ₃ CH ₂	81	90 (94)	10
9 ^b	(CH ₂) ₃ OH	H	100	87	13
10 ^b	PhCHOH	H	41	100	0
11 ^{b,c}	Ph	CH ₂ OH	90	90 (100)	10
12 ^{a,d}	CH ₃ (CH ₂) ₄	H	100	88 (4)	8
13 ^{a,e}	CH ₃ (CH ₂) ₄	H	100	82 (7)	11

Reaction conditions: Substrate (1.24 mmol), cat. (8 mg, 0.014 mol % Pd), THF, quinoline: Pd = 10⁴, 1.7 × 10⁻² M quinoline.

^a 3 bar H₂, 30 °C, 2 h; ^b 5 bar H₂, 50 °C, 2 h; ^c No quinoline added; ^d Lindlar catalyst (0.014 mol % Pd); ^e Pd Nanoselect catalyst, LF-200 (0.014 mol % Pd)

Interestingly when 4-octyne was tested under stronger conditions (50 °C, 5 bar H₂, 2 h, entry 5), 98% conversion was reached while maintaining full selectivity to the alkene. In the semi-hydrogenation of phenylacetylene and cyclohexylacetylene (Entries 6 and 7), lower conversion was measured for the aromatic alkyne (62 vs. 87%), while the alkene selectivity was similar for both substrates (ca. 95%). For 1-phenyl-butyne (Entry 8), 90% selectivity was obtained at 81% conversion.

In the hydrogenation of the terminal alkynols 4-pentyne-1-ol and 1-phenyl-2-propyn-1-ol (Entries 9 and 10), a similar behavior to that observed for the alkynes was evidenced since the alkynol bearing an aromatic ring was converted more slowly (41 vs. 100%).

These results demonstrated that this paper based catalytic system can provide excellent selectivity to the alkene product at high conversion. For instance, Jung et al reported the performance of palladium catalysts supported on carbon nanofibers and Pd/activated charcoal in the hydrogenation of 1-octyne and obtained selectivities towards 1-octene of 68 and 21% respectively at 97% of conversion.^[14] These values are inferior to

those described here using our paper based catalytic system. Using "his" polymer/paper based catalyst, Nikishima et al reported the hydrogenation of diphenylacetylene but obtained no selectivity towards the alkene.^[4c]

In order to compare the performance of the paper-based catalyst, two catalytic reactions were performed using 1-heptyne as substrate in the presence of commercial catalysts (Entries 12 and 13), namely the Lindlar catalyst (5 wt% Pd/CaCO₃, Pb poisoned) and the Pd Nanoselect catalyst (LF-200, 0.5 wt% Pd/TiS). Under these conditions, similar results were obtained in terms of activity and alkene selectivity for the commercial catalysts and the paper-based material reported here.

With these results in hand, the recyclability of the here described paper-based catalyst was tested in the semi-hydrogenation of 1-phenyl-2-propyne-1-ol during 5 consecutive runs (Figure 3). Between each reaction, washings with THF was performed prior to the next reaction. Excellent results in terms of alkene selectivity and conversion were obtained in the five runs (100% at 94% of conversion), thus evidencing the robustness of the catalyst under these conditions. ICP analysis of the organic phase after catalysis confirmed that no Pd leaching had taken place during these reactions, hence demonstrating that the anchoring of the Pd@CNT on the paper is an efficient approach for the preparation of stable and reusable catalysts. The stability of the catalyst was attributed to the strong interactions metal nanoparticles-carbon nanotubes,^[7, 15] at first as well as the carbon nanotube/cellulose irreversible adsorption^[16].

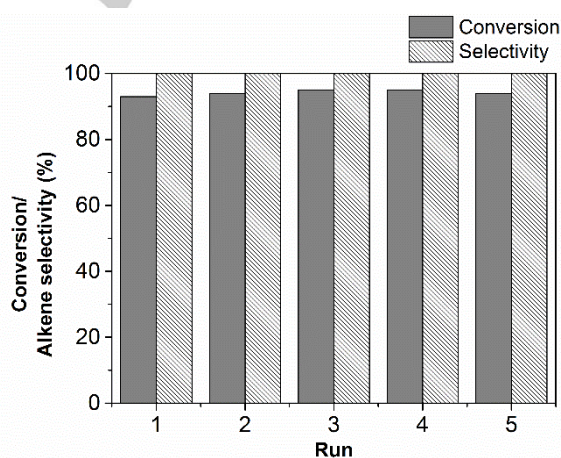


Figure 3. Recyclability of the paper catalyst in the hydrogenation of 1-phenyl-2-propyne-1-ol. Reaction conditions: 1.24 mmol substrate, cat. (8 mg, 0.014 mol % Pd), p H₂=5 bar, T=50°, THF, 2.5 h.

In conclusion, a new Pd nanocatalyst supported on paper was successfully prepared using MWCNTs as an interface. The catalyst was prepared by Pd₂(dba)₃ decomposition under H₂ in the presence of MWCNTs and PCy₃ as stabilizer, followed by their impregnation on paper. This new nanocatalyst was tested in the semi-hydrogenation of several internal and terminal alkyne and alkynol substrates and after optimisation of the reaction conditions, excellent selectivities at high conversions were obtained for all the substrates. Using 1-heptyne as substrate, similar performances were obtained with commercial catalysts

(Lindlar's and Pd-Nanoselect) under the same conditions. However, the recycling of our paper based material is more facile since no filtration is required. Furthermore, the new catalyst could be recycled 5 times without loss of activity nor selectivity. This simple and versatile approach is very attractive since it could easily scalable and also applied to other substrates such as textile,^[17] plastics,^[18] and rubber^[19].

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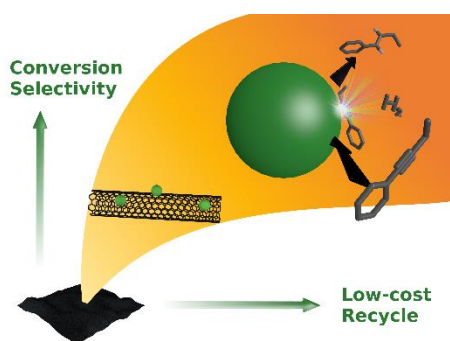
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