## 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 (CNT = carbon nanotubes) ink was herein explored. The resulting paper-based material provided excellent results in the semihydrogenation of alkynes and alkynols and could be recycled at least five times without loss of activity or selectivity.

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

Nanocatalysts are usually immobilized on oxides such as silica or alumina, on polymers, or on carbon materials.<sup>[3]</sup> However, the immobilization of selective catalysts onto cheap and easy-to-handle solid supports is still of general interest, and recently, alternative carriers such as textile, paper, and cotton were demonstrated to be very attractive.<sup>[4]</sup> 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.<sup>[4b]</sup> This organotextile was used in several reactions such as the acylation of phenols to the esters and in the desymmetrization of anhydrides with very good enantioselectivity. More recently, Nagashima and co-workers reported polycationic salt stabilized palladium nanoparticles immobilized on both cotton and

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paper as reusable catalysts for sequential cross-coupling and hydrogenation reactions.<sup>[4c]</sup> Conventional filter paper is of inherent interest as a catalyst support, as it is cost effective, biodegradable, accessible, and flexible. It, therefore, simplifies the handling of the catalyst, for example, by manipulation with tweezers, as well as the recycling process. Oleylamine-capped Pd nanoparticles absorbed on paper were reported to provide reusable catalysts for Suzuki cross-coupling and nitro-to-amine reduction.<sup>[4d]</sup> These results show that such supports can be efficient, although in these examples, the synthetic strategies were complex (covalent grafting of the catalyst)<sup>[4]</sup> or limited to a certain type of NP stabilizer to provide interactions with the support.<sup>[4c, d]</sup> To overcome this latter drawback, the use of an interface between the nanocatalyst and the support appears promising, as it would allow the utilization of any type of stabilizer. Carbon nanotubes present great potential for this role<sup>[5]</sup> owing to their chemical stability, suitable porous properties, and broad functionalization strategies (covalent and noncovalent).<sup>[6]</sup> In some cases, their structure also leads to metal-support interactions that can enhance the activity/selectivity of the catalysts.<sup>[7]</sup> In addition, multiwalled carbon nanotubes deposited by chemical vapor deposition on silicon chips followed by decoration with Pd to form a catalyst support membrane was previously reported.<sup>[8]</sup>

In the present communication, we describe the use of carbon nanotubes (CNTs) as an interface between the metal NPs and the support: the palladium nanoparticles were first grown onto the nanotubes (Pd@CNT), and the resulting hybrid material was subsequently anchored onto paper by simple painting of a Pd@CNT ink (Figure 1).<sup>[9]</sup> This general approach is simple, versatile, and easily scalable (by printing process of the ink). The paper-based nanocatalyst was applied in the semihydrogenation of alkynes and alkynols; excellent catalytic performance was observed and the nanocatalyst could be used over at least five consecutive runs without loss of either activity or selectivity. The Pd nanoparticles were synthesized by a one-pot method involving the decomposition of Pd<sub>2</sub>(dba)<sub>3</sub> (dba = dibenzylideneacetone) under an atmosphere of H<sub>2</sub> in the presence of tricyclohexylphosphine (PCy<sub>3</sub>) and multiwalled carbon nanotubes (MWCNTs) (Figure 1 a).<sup>[10]</sup> TEM analysis of the resulting hybrid material (Figure 2a) evidenced the homogeneous deposition of small PdNPs with a narrow size distribution [(2.4 $\pm$ 0.9) nm] onto the surface of the CNTs. Thermogravimetric analysis revealed that these Pd@CNT hybrids exhibited a content of palladium of approximately 35 wt% (Figure S1 in the Supporting Information).



**Figure 1.** General approach for the preparation of the paper-based nanocatalyst: a) nanoparticles are grown on the surface of the CNTs to afford the Pd@CNT hybrid, b) the hybrid is mixed with a surfactant to produce the Pd@CNT ink, c) a filter paper is painted with Pd@CNT, d) the paper catalyst is used for the semihydrogenation of alkynes, e) the catalyst is washed and recycled over several reactions.





Figure 2. a) TEM image of Pd@CNT and b) ESEM image of the paper-based nanocatalyst (the red spots correspond to PdNPs deposited onto MWCNTs). Scale bars = a) 20 nm, b) 500 nm.

Subsequently, the preparation of the paper-based nanocatalyst was performed manually by painting a conventional filter paper. First, an ink was prepared by sonicating an aqueous mixture of Pd@CNT and sodium dodecylbenzenesulfonate (SDBS) (Figure 1 b). The resulting suspension was then painted onto the paper to afford the paper-based nanocatalyst (Figure 1 c).<sup>[9]</sup> Figure 2 b displays the ESEM/EDX (environmental scanning microscopy/energy-dispersive X-ray spectroscopy) micrograph of the paper, for which the homogeneous dispersion of Pd (red spots) at the surface of the cellulose fibers is evidenced. Inductively coupled plasma (ICP) analysis of the paper painted with 3, 7, and 10 layers of the Pd@CNT ink revealed Pd contents of 0.15, 0.23, and 0.31 wt%, respectively. Notably, the amount of Pd could be tuned by varying the number of ink layers. The range of Pd loadings in these materials is comparable to that of the method reported by Nagashima.<sup>[4c]</sup>

The paper-based catalyst painted with 7 layers was employed in the semihydrogenation of alkynes and alkynols, which is a process of industrial relevance.<sup>[3]</sup> 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 (0.1–1.0 MPa) and heated (30/50 °C) under stirring. After the reaction, the catalytic material was removed by using tweezers, and the organic phase was analyzed by GC–MS.

The experimental conditions (pressure, temperature, and time) were initially optimized for a series of terminal and internal alkynes and alkynols (Tables S1–S3).<sup>[11]</sup> If necessary, quinoline was used as an additive, and its concentration was optimized for each substrate.<sup>[12]</sup> Excellent selectivity to alkenes at high conversions was achieved for both alkyne and alkynol substrates by using this new paper-based catalyst. Milder reaction conditions were required for the partial hydrogenation of terminal alkynes (0.3 MPa H<sub>2</sub>, 30 °C) than for the partial hydrogenation of internal alkynes or alkynols (0.5 MPa H<sub>2</sub>, 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 (Table 1, entries 1 and 2), excellent selectivities were obtained for heptyne and octyne at full conversions (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 a substrate (Figure S4). Upon comparing the reactivities of 1-octyne, 2-octyne, and 4-octyne (Table 1, entries 2–4), a decrease in the conversion from 100 to 56% was observed if the triple bond was internal, whereas the alkene selectivity increased from 89 to 100%. These results can be related to accessibility issues of the substituted triple bonds, as previously proposed.<sup>[13]</sup>

Interestingly upon testing 4-octyne under stronger conditions (50 °C, 0.5 MPa H<sub>2</sub>, 2 h; Table 1, entry 5), 98% conversion was reached and full selectivity to the alkene was maintained. In the semihydrogenation of phenylacetylene and cyclohexylacetylene (Table 1, entries 6 and 7), lower conversion was measured for the aromatic alkyne (62 vs. 87%), whereas the alkene

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Table 1. Substrate scope for the selective hydrogenation of alkynes and alkynols catalyzed by the paper-based catalyst. <sup>[a]</sup>								
$R^{1} \xrightarrow{\qquad} R^{2} \xrightarrow{\qquad} H_{2}/Cat \qquad R^{1} \xrightarrow{\qquad} R^{2} + \underbrace{\qquad} R^{2} \xrightarrow{\qquad} R^{2}$								
			cis-A	trans-A	В			
Entry	R <sup>1</sup>	R <sup>2</sup>	Conv.	Sel	elect. [%]			
			[%]	A (isomer%	or cis%)	В		
1 <sup>[b]</sup>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub>	Н	100	94 (2)		4		
2 <sup>[b]</sup>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	Н	100	89 (4)		7		
3 <sup>[b]</sup>	$CH_3(CH_2)_4$	CH₃	66	95 (98)		1		
4 <sup>[b]</sup>	$CH_3(CH_2)_2$	$CH_3(CH_2)_2$	56	100 (96)		0		
5 <sup>[c]</sup>	$CH_3(CH_2)_2$	$CH_3(CH_2)_2$	98	100 (95)		0		
6 <sup>[b]</sup>	Ph	н	62	94		6		
7 <sup>[b]</sup>	Су	н	87	95		5		
8 <sup>[c]</sup>	Ph	$CH_3CH_2$	81	90 (94)		10		
9 <sup>[c]</sup>	(CH <sub>2</sub> ) <sub>3</sub> OH	Н	100	87		13		
10 <sup>[c]</sup>	PhCHOH	Н	41	100		0		
11 <sup>[c,d]</sup>	Ph	CH₂OH	90	90 (100)		10		
12 <sup>[b,e]</sup>	$CH_3(CH_2)_4$	Н	100	88 (4)		8		
13 <sup>[b,f]</sup>	$CH_3(CH_2)_4$	н	100	82 (7)		11		
[a] Reaction conditions: substrate (1.24 mmol), catalyst (8 mg, 0.014 mol % Pd), THF, quinoline/Pd = $10^4$ , $1.7 \times 10^{-2}$ M quinoline. [b] 0.3 MPa H <sub>2</sub> , 30 °C, 2 h. [c] 0.5 MPa H <sub>2</sub> , 50 °C, 2 h. [d] No quinoline was added. [e] Lindlar catalyst (0.014 mol % Pd). [f] Pd Nanoselect catalyst, LF-200 (0.014 mol % Pd).								

selectivity was similar for both substrates ( $\approx$ 95%). For 1-phenyl-butyne (Table 1, 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 (Table 1, entries 9 and 10), a similar behavior to that observed for the alkynes was evidenced, as the alkynol bearing an aromatic ring was converted more slowly (41 vs. 100%).

These results demonstrated that this paper-based catalytic system could 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 1octyne and obtained selectivities towards 1-octene of 68 and 21%, respectively, at 97% of conversion.<sup>[14]</sup> These values are inferior to those described here using our paper-based catalytic system. Nikishima et al. reported the hydrogenation of diphenylacetylene by using a polymer/paper-based catalyst but obtained no selectivity towards the alkene.<sup>[4c]</sup>

To compare the performance of the paper-based catalyst, two catalytic reactions were performed by using 1-heptyne as the substrate in the presence of commercial catalysts (Table 1, entries 12 and 13), namely, the Lindlar catalyst (5 wt% Pd/CaCO<sub>3</sub>, 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 both the commercial catalysts and the paper-based material reported herein.

With these results in hand, the recyclability of the herein-described paper-based catalyst was tested in the semihydrogenation of 1-phenyl-2-propyne-1-ol over five consecutive runs





**Figure 3.** Recyclability of the paper catalyst in the hydrogenation of 1-phenyl-2-propyne-1-ol. Reaction conditions: substrate (1.24 mmol), catalyst (8 mg, 0.014 mol% Pd),  $H_2$  (0.5 MPa), 50 °C, THF, 2.5 h.

(Figure 3). Between each reaction, washing 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% selectivity at 94% of conversion), which thus evidences 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, which hence demonstrates that the anchoring of Pd@CNT on the paper is an efficient approach to prepare stable and reusable catalysts. The stability of the catalyst was attributed to strong interactions between the metal nanoparticles and the carbon nanotubes,<sup>[7, 15]</sup> as well as irreversible adsorption of the carbon nanotubes onto cellulose.<sup>[16]</sup>

In conclusion, a new Pd nanocatalyst supported on paper was successfully prepared by using multiwalled carbon nanotubes as an interface. The catalyst was prepared by decomposition of  $Pd_2(dba)_3$  under an atmosphere of  $H_2$  in the presence of multiwalled carbon nanotubes and tricyclohexylphosphine as a stabilizer, followed by their impregnation on paper. This new nanocatalyst was tested in the semihydrogenation of several internal and terminal alkyne and alkynol substrates, and after optimization of the reaction conditions, excellent selectivities at high conversions were obtained for all substrates. Using 1-heptyne as a substrate, similar performances were obtained with commercial catalysts (Lindlar and Pd-Nanoselect catalysts) under the same conditions. However, recycling of our paper-based material is more facile, as no filtration is required. Furthermore, the new catalyst could be recycled five times without loss of activity or selectivity. This simple and versatile approach is very attractive, as it is easily scalable and could also be applied to other substrates such as textiles,<sup>[17]</sup> plastics,<sup>[18]</sup> and rubbers.<sup>[19]</sup>

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## COMMUNICATIONS

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