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## **Confinement of Metal Nanoparticles in Carbon Nanotubes**

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The effect of several parameters that include carbon nanotube (CNT) pretreatment and diameter, and the nature of the metal (Co, Ru, Pd), the metal precursor (nitrate, chloride, organometallic complexes), and the solvent on the filling yield of metallic nanoparticles in CNT channels is reported. The obtained results show that it is possible to modulate the filling yield between 10 and 80% by controlling the CNT opening and playing on the molecular recognition of the inner/outer surfaces by the metal molecular precursor. Interestingly, the best filling yields

#### Introduction

The confinement of metal nanoparticles (NPs) in carbon nanotubes (CNTs) has gained an increasing amount of attention because of potential applications in catalysis, data storage, and electronic devices. By using the spatial restriction effect of CNT channels, a variety of nanomaterials, even of sub-nanometer size, can be synthesized. These materials would be usually intrinsically unstable, particularly under elevated temperature and pressure, or difficult to obtain under mild conditions.<sup>[1]</sup> Additionally, modified adsorption, diffusion, structural, and chemical properties have been reported for a variety of species confined in CNTs compared to their counterparts either in the bulk or deposited on the outer CNT walls.<sup>[1a,2]</sup> A stronger adsorption onto the CNT inner surface was reported for CO, H<sub>2</sub>, alkanes, and alkenes,<sup>[3]</sup> which has opened the way to selective adsorption/separation processes.<sup>[4]</sup> The diffusion of various molecules, which include  $N_2^{[5]}$  and  $H_2O_7^{[6]}$  inside individual CNTs was reported to be faster than their bulk diffusion. y-Fe NPs with a face-centered cubic (fcc) crystal structure, known to be stable between 1185-1667 K in the bulk, retained their stability at room temperature if confined in  $\ensuremath{\mathsf{CNTs}}^{\ensuremath{\mathsf{[7]}}}$  Confined cobalt nanorods showed an fcc instead of a stable hexagonal structure.<sup>[8]</sup> The reduction of iron oxide NPs confined in CNT channels was found to be facilitated with respect to the particles located on the outer walls.<sup>[9]</sup> As a result of these confinement effects, metal NPs filled inside CNTs usually show better catalytic performances than those loaded on the outer surface.[1a, c, d, 10] Indeed, confinement effects can affect chemical reactions through a host of aspects, such as changes in the thermodynamic state of the system because of interactions with inside

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201300527. have been obtained on nitric acid oxidized nanotubes; a treatment often used for the preparation of most CNT-supported metal catalysts. The confined nanoparticles systematically show a smaller particle size than those supported on the external surface. All the prepared samples were tested for the selective hydrogenation of cinnamaldehyde, and clear correlations were established between the catalytic performances and the filling yields.

walls, selective gas adsorption, and geometrical constraints that affect the reaction mechanism.<sup>[11]</sup> As these effects are expected to be enhanced if the CNT inner diameter is reduced,<sup>[4a,9b,12]</sup> the preparation of NPs selectively localized inside small-diameter CNTs is a prerequisite to study this phenomenon.

To achieve maximum confinement, wet chemistry appears to be the most simple, versatile, and up-scalable method.<sup>[13]</sup> However, the capillary effect of CNTs depends on surface functionalization and CNT diameters. CNTs with internal diameters <10 nm are usually filled to a lesser extent or even remain empty after wet impregnation.<sup>[14]</sup> Reported methods for filling include: 1) wet impregnation assisted by ultrasound by using cut CNTs,<sup>[15]</sup> 2) two-step biphasic impregnation,<sup>[16]</sup> 3) impregnation and selective washing,<sup>[17]</sup> 4) the use of supercritical  $CO_{2}$ ,<sup>[18]</sup> and 5) molecular recognition.<sup>[19]</sup> The reported filling yields, which are commonly measured either by conventional 2D TEM, performed with<sup>[20]</sup> or without sample tilting, or by electron tomography<sup>[21]</sup> ranged between 70–90%. Among the preparation methods cited, only the first one, originally developed by the group of Bao, has been applied for the filling of small-diameter (<10 nm) CNTs with  $Ru_{,}^{[22]}$   $Fe_{,}^{[9,23]}$   $Cu_{,}^{[12a]}$ MnO<sub>2</sub>,<sup>[24]</sup> TiO<sub>2</sub>,<sup>[25]</sup> and Rh<sup>[26]</sup> NPs. The first step of this simple procedure involves CNT oxidation with HNO<sub>3</sub> to open the CNT tip and to create oxygen surface functional groups.<sup>[27]</sup> This surface oxidation reaction is also used for the preparation of most CNT-supported catalysts,<sup>[1b]</sup> which often show better performances than their counterparts supported on other supports, which include carbonaceous ones.<sup>[28]</sup> As most of the studies that deal with CNTs for catalysis have neglected the possibility of confinement of the active phase in the CNT inner cavity, we wonder about the possible role of unidentified confinement effects on the catalytic results.

We report herein the first parametric study that deals with the confinement of metal NPs in CNTs. We studied the influence of several parameters such as CNT pretreatment and di-

are presented in Figure S2. Ballmilling in air permits the opening of a few CNTs (a moderate increase of  $S_{BET}$ ), introduces low

amounts of oxygenated groups

de-

has

and

(temperature-programmed

TPD),

a marked influence on the multiwalled CNT (MWCNT) length. Although no statistical analysis

was performed, it can be stated

that the majority of the tube

ends in **CNT2** are not open and collapsed; these ends are closed

by bending one side of the wall

to the opposing one. Such results are in accordance with reported data.<sup>[30,31]</sup> The decrease of

ameter, and the nature of the metal (Co, Ru, Pd), metal precursor (nitrate, chloride, organometallic complexes), and solvent on the filling yield. We also investigated the influence of NP confinement on the performance for cinnamaldehyde hydrogenation, a reaction for which confinement effects have been already reported.

Table 1. Specific surface area, pore volume, and Raman data of the CNT supports.							
	i.d./e.d. <sup>[a]</sup> [nm]	Length [µm]	$S_{BET}$ [m <sup>2</sup> g <sup>-1</sup> ]	V <sub>pore</sub> [cm <sup>3</sup> g <sup>-1</sup> ]	$I_{\rm D}/I_{\rm G}$	CO <sub>2</sub> [μmc	TPD $blg^{-1}$ CO $[\mu molg^{-1}]$
CNT0	5.5:10.9	1–2	240	2.55	1.49	62	211
CNT1	5.5:10.9	1–2	365	0.89	1.53	1296	2132
CNT2	5.5:10.9	0.5-0.8	280	1.14	1.52	437	871
CNT1HT	5.5:10.9	1–2	390	0.86	1.74	-	-
CNT2HT	5.5:10.9	0.5-0.8	288	1.04	1.52	-	-
CNT3	40:70	0.5–4	38	0.15	0.87	295	642
[a] Ratio of internal to external diameter.							

#### **Results and Discussion**

#### Characterization of catalyst supports

The purified CNTs (CNT0) present a specific surface

area of 240 m<sup>2</sup>g<sup>-1</sup>, a mean internal diameter of 5.5 nm, and a mean external diameter of 10.9 nm (Figure S1, Supporting Information). Their thermogravimetric analysis (TGA) profile under air shows a decomposition temperature of 640 °C, and a purity > 98% (Figure S2). **CNT0** has been subjected to different treatments (Scheme 1) to evaluate the influence of CNT opening and surface chemistry on the filling yield. oxygen-containing surface functional groups.<sup>[30]</sup> **CNT1** and **CNT2** were then treated at 900 °C under Ar for **CNT1** or  $Ar/H_2$  for **CNT2** to remove the oxygen surface functional groups to produce **CNT1HT** and **CNT2HT**, respectively. Selected characteristics of the prepared supports are shown in Table 1.

The  $N_2$  adsorption isotherms and pore size distribution for the five samples are given in Figure S3, and the TGA profiles

sorption,

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Scheme 1. Different treatments performed on the pristine CNTs.

**CNT1** was obtained by nitric acid oxidation of **CNT0**. Details of the mechanism of  $HNO_3$  oxidation of CNTs have been reported elsewhere.<sup>[27]</sup> Briefly, this reaction involves the initial rapid formation of carbonyl groups, which are consecutively transformed into phenol and carboxylic groups.  $HNO_3$  oxidation also allows an increase of the BET surface area ( $S_{BET}$ ) because of CNT tip opening.

With large-diameter CNTs such as **CNT3**, which present exposed edges along the entire interior and exterior surfaces, it has been proposed that prolonged reaction with HNO<sub>3</sub> contributes to both endohedral and exohedral functionalization.<sup>[16]</sup> In the case of small-diameter CNTs, we recently evidenced that 3 h contact in boiling HNO<sub>3</sub> is not enough for endohedral functionalization.<sup>[29]</sup> Thus, we can expect both endo- and exohedral –COOH functionalization for the large-diameter, open-ended **CNT3**,<sup>[19]</sup> and only exohedral –COOH functionalization for the small-diameter **CNT1**. **CNT2** was produced by ball-milling of **CNT0** in air. Ball-milling reduces the CNT length from 1–2 µm to 500–800 nm (Figure S1) and introduces a limited amount of

the pore volume should be connected to the decrease of the CNT length. Such shortening would contribute to the formation of MWCNT agglomerates with a densely packed structure (Figure S1). Thus, a study by Kim et al. showed that the grinding of CNTs resulted in shortened and densely packed CNTs with increased cleavage as a result of increased grinding time.<sup>[32]</sup>

Nitric acid oxidation allows a better opening of **CNT0**, as evidenced by the marked increase of the  $S_{BET}$  value of **CNT1** and by the increase of the contribution of the pores that range between 2–9 nm (Figure S3). The decrease of the pore volume is connected to the formation of a hydrogen bond network between the –COOH surface functional groups, which contributes to the formation of dense MWCNT agglomerates. The high-temperature treatments performed on **CNT1** and **CNT2** did not significantly modify CNT opening as reflected by the  $S_{BET}$  values.

The Raman spectroscopic data, which yield information about the purity and defects of MWCNTs,<sup>[33]</sup> show that the

high-temperature treatment performed under Ar (**CNT1HT**) contributes to the introduction of defects, presumably vacancies, in the carbon structure. Such an effect of high-temperature treatment on oxidized CNTs has been reported.<sup>[19]</sup>

TPD profile deconvolution (Figure S4) shows that the groups present on the **CNT1** external surface are carboxylic acids (1020  $\mu$ mol g<sup>-1</sup>), lactone (110  $\mu$ mol g<sup>-1</sup>), carboxylic anhydride (165  $\mu$ mol g<sup>-1</sup>), phenol (918  $\mu$ mol g<sup>-1</sup>), and carbonyl/quinone groups (920  $\mu$ mol g<sup>-1</sup>). At 900 °C, most of the oxygen surface functional groups have disappeared (Figure S4). For **CNT1HT**, the exposure to air will not contribute to significant reoxidation as checked independently in our laboratory, and for **CNT2HT**, a surface passivation with C–H bond formation is expected.<sup>[34]</sup> The TGA profiles (Figure S2) are in accordance with these observations.

To summarize, we produced different CNTs with differences in their opening and surface chemistry. The confinement of metal NPs in CNTs will be mainly governed by two parameters: 1) CNT opening (tip opening but also the removal of graphene layers that could have grown perpendicularly to the tube axes (bamboo-type structure)), and 2) molecular surface recognition, indeed during the impregnation procedure the metallic precursor should present a higher affinity for the inner than the outer surface. The channels of **CNT1** and **CNT3** are well opened and should allow a higher filling yield than the other samples. A difference in the inner/outer surface chemistry that may impact the filling yield can be expected for **CNT1** (only endohedral chemical functionalization), **CNT1T** (higher concentration of defects on the external surface induced by group removal), and **CNT2HT** (C–H external surface passivation).

## Influence of CNT pretreatment and choice of the metal on confinement

Owing to the large number of samples prepared, and to the fact that electron tomography and conventional 2D-TEM with sample tilting are time-consuming methods, we measured the filling yields from conventional 2D-TEM micrographs. If we consider that the internal diameter of Nanocyl nanotubes is half their external diameter, the filling yield was calculated as follows [Eq. (1)]:

$$Yield = 2\left(\frac{\text{number of particles inside}}{\text{total number of particles}} \times 100\right) - 100$$
(1)

The yield was calculated for more than 300 particles deposited on/in 50 different CNTs. Although this method is not very accurate, it is convenient for comparison purposes. Additionally, we checked one sample independently (see below) to see that the results are consistent with that obtained by electron tomography. The influence of CNT pretreatment on confinement was evaluated for three metals, Co, Ru, and Pd, by using wet impregnation and nitrate salts as the NP precursor (5 wt% theoretical loading). Acetone was chosen as the solvent because its surface tension ( $25.2 \text{ mNm}^{-1}$ ) is far below the cut-off value for wetting ( $180 \text{ mNm}^{-1}$ ) and can fill the CNT channels by capillary force. The results of the influence of CNT pretreat-

Table 2. Metal loading, NP size, and filling yields for the Ru, Co, and	Pd
systems on the different CNT supports.	

Support	Metal Ru	loading Co	[wt %] Pd	NP si Ru	ze [nn Co	n] Pd	Filling y Ru	yield [%] Co	Pd
CNT0 CNT1 CNT2 CNT1HT	2.17 0.99 2.01 1.41	3.17 2.72 3.28 2.94	3.25 1.24 3.08 1.64	2.21 1.02 1.87 1.25	3.48 2.72 3.25 2.88	4.15 1.15 4.01 2.48	$19\pm7$ $73\pm9$ $48\pm5$ $60\pm9$ $60\pm9$	$15 \pm 8$ $64 \pm 9$ $38 \pm 7$ $53 \pm 8$ (2 + 10)	$13\pm 8$ $72\pm 10$ $35\pm 8$ $58\pm 9$ $c_{0}+7$

ment on metal loading, NP size, and filling yield are reported in Table 2. The TEM analyses and particles size distribution are given in Figures S5–S7.

#### Metal loading

The measured metal loading was lower than the theoretical value and followed the order  $Co \approx Pd > Ru$ . For a given metal, the loading also depends on the CNT pretreatment. Surprisingly, regardless of the metal used, we find a decrease of metal loading with the increase of the  $S_{BET}$  value of the support (Figure S8), and a decrease of the metal loading with the increase of the filling yield (Figure 1). This phenomenon is more pronounced for Ru and Pd precursors than for Co. For the higher filling yields obtained on CNT1, the two neutral Ru and Pd precursors ([Ru(NO)(NO<sub>3</sub>)<sub>3</sub>] (Ru1) and [Pd(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (Pd1))<sup>[35]</sup> should be less reactive towards the external, -COOH-decorated surface of CNTs compared to the cationic Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Co1) species. If the presence of -COOH groups on carbon surfaces have been often cited as possible anchoring sites for the metal precursor, it should depend on the reactivity of the precursor. This can explain the higher metal loading and the lower filling yield obtained for CNT1 with respect to Ru and Pd.

#### Nanoparticle size

The mean NP size follows the order Ru < Pd  $\approx$  Co. This order is consistent with the adsorption energy of metal adatoms on graphite: Ru (4.43 eV) > Co (3.64 eV) > Pd (1.90 eV).<sup>[36]</sup> For a given metal, the mean NP size decreases with the increase of the filling yield (Figure S9).

This is because the mean size of NPs located inside the CNT channel (NP<sub>in</sub>) size is systematically smaller than the mean size of NPs located on the external surface (NP<sub>out</sub>). We measured these diameters by conventional TEM for the catalysts prepared on **CNT1** and **CNT2** (Figures 2 and 3). The phenomenon is more pronounced for **CNT2** than **CNT1**, which indicates a different external surface chemistry. We also confirmed the obtained data by electron tomography analyses on Ru/**CNT1** (Figure S10). Although all our efforts to find a facile correlation between this divergence of diameters and the filling yield failed, a specific study devoted to this aspect of our work deserves to be performed.

This effect of confinement on NP size could have two origins: 1) changes of concentration of the precursor or  $H_2$  partial

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Figure 1. Influence of filling yield on metal loading.

pressure in the inner cavity compared to the rest of the medium and/or 2) a different surface chemistry of the two surfaces (convex/concave) that could impact the nucleation step and/or NP stability.

#### Filling yield

Finally, the filling yield follows the same trend regardless of the metal used: **CNT1** > **CNT1HT**  $\approx$  **CNT2HT** > **CNT2** > **CNT0**. No significant influence of the nature of the metal on the filling yield was observed. As already stated, the filling yield should depend on the CNT opening and thus on the *S*<sub>BEP</sub> and on surface molecular recognition and thus on CNT surface chemistry. The higher yields obtained on **CNT1** compared to **CNT0** and **CNT2** has been attributed to the CNT opening (Figure 4). The effect of the high-temperature treatment should be more pronounced on the CNT surface chemistry than on their specific surface area. A decrease of the filling yield upon high-temperature treatment of HNO<sub>3</sub>-oxidized CNTs has already been reported for Ru catalysts prepared from RuCl<sub>3</sub>.<sup>[22c]</sup> The authors attri-

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bute this effect to the presence of a larger amount of external defects on the heat-treated sample that act as anchoring sites for NPs. In our case, this could contribute to explain the lower filling yield obtained on **CNT1HT** ( $I_D/I_G$  Raman ratio = 1.74) than on **CNT1** ( $I_D/I_G$  Raman ratio = 1.53). In the case of **CNT2**, the effect of the high-temperature treatment is the opposite. The difference should arise from the treatment performed under an H<sub>2</sub>/Ar mixture. Under such conditions, the passivation of the external surface by the formation of C–H bonds should decrease the amount of anchoring sites on the external surface.

# Influence of solvent, metal precursor, and CNT diameter on confinement

Four Ru precursors, [Ru(NO)(NO<sub>3</sub>)<sub>3</sub>] (Ru1), [Ru<sub>3</sub>(CO)<sub>12</sub>] (Ru2), RuCl<sub>3</sub> (**Ru3**), and [Ru(COD)(COT)] ((1,5-cyclooctadiene)(1,3,5-cyclooctatriene)ruthenium(0), Ru4), and two Pd precursors, Pd-(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> (Pd1) and [Pd<sub>2</sub>(dba)<sub>3</sub>] (tris(dibenzylideneacetone)dipalladium(0), Pd2), have been used in combination with the CNT1 support. In the case of Ru1/CNT1, three different solvents, acetone, isopropanol, and water have been used. These solvents show different surface tensions and viscosities: 1) surface tension at 25 °C [mNm<sup>-1</sup>]: acetone (23), isopropanol (23.3), and water (72.7), well below the critical surface tension of CNTs, 2) dynamic viscosity at  $25 \degree C$  [mN s m<sup>-2</sup>]: acetone (0.31), isopropanol (2.04), and water (0.89), and 3) kinematic viscosity at 25 °C [m<sup>2</sup>s<sup>-1</sup>]: acetone (0.39), isopropanol (2.61), and water (0.89). The metal loadings, NP size and filling yields are given in Table 3. TEM observations and NP size histograms are given in Figures S11–S13.

Table 3. Metal loading, NP size, and filling yields for the Ru and Pd systems on CNT1.							
Precursor/solvent	Metal loading [wt %]	NP size [nm]	Filling yield [%]				
Ru1/acetone (0.23 $\%$ H <sub>2</sub> O)	0.99	1.02	$73\pm9$				
Ru1/acetone (1 % H <sub>2</sub> O)	0.97	1.01	$77\pm10$				
<b>Ru1</b> /acetone (10% H <sub>2</sub> O)	1.00	1.02	$77\pm10$				
Ru1/acetone (20% H <sub>2</sub> O)	0.99	1.03	$74\pm10$				
Ru1/isopropanol	1.05	1.04	$70\pm9$				
Ru1/water	1.10	1.16	$61\pm8$				
Ru2/acetone	2.83	3.80	$40\pm\!6$				
Ru3/isopropanol	1.90	1.42	$58\pm10$				
Ru4/acetone	1.3	1.12	$52\pm8$				
Pd1/acetone	1.24	1.15	$72\pm10$				
Pd2/toluene	2.20	3.48	$58\pm7$				
Ru1Pd1/acetone	2.17 (1.33 Pd)	1.12	$73\pm9$				

The solvent viscosity does not impact the filling yield, at least not in the investigated range. A lower filling yield was observed in water, which is consistent with the higher surface tension of this solvent. The choice of the solvent has a limited impact on NP size and metal loading. The obtained results also show that the nuclearity of the precursor and the nature of the ligands and/or the metal oxidation state play a significant role on metal loading, NP size, and filling yield. Generally, pre-

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Figure 2. TEM micrographs and NP size distribution ( $NP_{in}/NP_{out}$ ) for a) Ru/CNT1, b) Co/CNT1, c) Pd/CNT1, and d) the mean NP size distribution for the three catalysts.



Figure 3. TEM micrographs and NP size distribution ( $NP_{in}/NP_{out}$ ) for a) Ru/CNT2, b) Co/CNT2, c) Pd/CNT2, and d) mean NP size distribution for the three catalysts.

cursors with a higher nuclearity, such as dimers (**Pd2**) or trimers (**Ru2**) allow higher metal loadings and a larger particle size to be reached. The use of these precursors, for which the metal is in the zero oxidation state in a pseudo-octahedral en-

the inner surface.<sup>[16]</sup> To confirm this hypothesis we performed experiments at 1, 10, and 20 wt% water in acetone (TEM images are shown in Figure S14). A moderate increase of the yield was observed for 1–10 wt%  $H_2O$ , which corresponds to

vironment, induces a decrease of the filling yield. In the coordination-compound-functionalization of CNTs, the  $\pi$  orbitals of the CNTs should overlap with the vacant  $d_{\pi}$  orbitals of the metal to result in efficient hexahapto  $(\eta^{6})$  complexation of the graphene sheet with transition metals; this mode of bonding is expected to exert the minimum perturbation of the structural integrity of the sp<sup>2</sup>-hybridized C atoms.[33] It seems reasonable to propose that the reactivity of the metal(0) precursors with the perfect inner CNT surface should be lower than that of the other precursors that show a +3 oxidation state and easily available coordination sites. Indeed, in the case of Ru2 and Pd2, the reaction with the graphene surface is preceded by ligand dissociation. Instead, a higher reactivity of the metal(0) precursors towards the external -COOH-decorated CNT surface is proposed, possibly by an oxidative addition. The low filling yields achieved with Ru4, a very reactive Ru<sup>0</sup> compound, supports this hypothesis. On the other hand metal(II) and metal(III) complexes are expected to be more reactive towards the internal surface as coordination will increase the electronic density on the metal, rather than with the external -COOH groups, as the oxidative addition on metal(II) or (III) is not favorable. Thus, if the presence of surface -- COOH groups is often associated with potential anchoring sites for the metal precursor, our study showed that it depends on the precursor reactivity. Additionally, it is possible that -COOH group hydration (the water content of acetone is 0.23 wt%) lowers their reactivity and displaces the thin organic solution film from the outer to



**Figure 4.** Influence of CNT BET surface area on the filling yield (the reported filling yields are average values for the Ru, Pd, and Co catalysts).

20–200 equivalents of  $H_2O$  relative to the –COOH surface functional groups.

Interestingly, mixing two precursors to produce a bimetallic catalyst (Ru1Pd1/CNT1) has no significant effect on the filling yield. Finally, we investigated the effect of CNT diameter on the filling yield. The Ru1Pd1/CNT3 catalyst shows a metal loading of 3.18% (2.0% Pd), a mean NP size of 2.35 nm, and a filling yield of 84%. For CNT3, even if the existence of exo-/ endohedral -- COOH functionalization limits the surface molecular recognition, the increase of the CNT internal diameter allows the filling yield to be improved.[35] To further support the importance of surface molecular recognition, we transformed the -COOH groups of CNT3 into long (16 C atoms) amide groups to produce CNT4. This was realized by reacting CNT3 with thionyl chloride, and hexadecylamine (HDA), as described elsewhere.<sup>[19]</sup> It is expected that this functionalization will mainly affect the external surface because of steric hindrance of the long HDA molecules. In that case, the external surface of the large-diameter CNT4 is passivated by long alkyl chains, and the filling yield increases to 92% (Figure 5). The metal loading of Ru/CNT4 is 3.08% (1.81% Pd), and the mean NP size is 2.27 nm. The obtained results show that besides the CNT opening, surface molecular recognition is an important aspect to take into consideration in improving the filling yield of CNTs.

#### Hydrogenation of cinnamaldehyde

One of the first reported applications of CNTs in heterogeneous catalysis was their use as supports for Ru NPs in the hydrogenation of cinnamaldehyde (CAL).<sup>[37]</sup> CAL contains both a C=C and a C=O bond in an  $\alpha$ , $\beta$ -unsaturated arrangement. Depending on which of the bonds are activated, hydrocinnamaldehyde (HCAL), cinnamyl alcohol (COL), or phenyl propanol (HCOL) can be produced. CNT-confined Pd,<sup>[38]</sup> PtRu,<sup>[19]</sup> and Au<sup>[39]</sup> NPs have shown high catalytic performances in this reaction. Pd is highly selective for HCAL, but not active for COL formation. Tessonnier et al. reported the confinement effect of Pd NPs deposited on the inner walls of large-diameter CNTs (50 nm internal diameter) for the selective hydrogenation of CAL to HCAL.<sup>[38]</sup> Zhang et al. have shown that gold NPs partially confined in the cavity of small-diameter CNTs (2–5 or 5– 10 nm internal diameter) show a striking enhancement of cata-



Figure 5. TEM micrographs and particle size distribution of a) Pd1Ru1/CNT3 and b) Pd1Ru1/CNT4.

lytic activity compared with those located on the outer surface. The chemoselectivity of the partially confined Au catalyst seems unique as competitive hydrogenation at the conjugated C=O bond into COL is avoided, which allows 90% selectivity for HCAL.<sup>[39]</sup> Bimetallic PtRu NPs have been selectively confined inside or deposited outside large-diameter CNTs (50 nm internal diameter), and a remarkable influence of the NP location on catalyst performance has been evidenced.<sup>[19]</sup> The confined PtRu NPs display a significantly higher selectivity and activity for COL formation.

The catalytic performances of the Ru, Co, and Pd supported catalysts reported in Table 2 have been evaluated for CAL hydrogenation at 100 °C and 20 bar of H<sub>2</sub>. The results are reported in Figure 6, in which the turnover frequency (TOF)  $[h^{-1}]$  and selectivity at isoconversion, Ru (COL, 88% conversion), Co (COL, 35% conversion), and Pd (HCAL, 100% conversion), are reported.

Although parameters other than confinement, such as the NP size or the CNT surface chemistry, can affect the selectivity and the activity of these catalysts for CAL hydrogenation,<sup>[40]</sup> Figure 6 clearly shows an influence of the filling yield on the catalytic performances. The effect is more pronounced for the Ru and Pd catalysts than for the Co one. Ru and Pd are the most active catalysts. As expected, Ru is the most selective metal for COL production, and the major product of the reaction is HCOL ( $\approx 60\%$ ). The Pd catalysts are the most selective for HCAL synthesis, and the other product of the reaction is HCOL. The use of the bimetallic **Pd1Ru1**/CNT catalyst allows the COL selectivity to be increased to 38% (HCOL 40%, HCAL



Figure 6. Selectivity and TOF of the prepared a) Ru, b) Co, and c) Pd catalysts.

22%) with a TOF of 240 h<sup>-1</sup>. Regardless of the CNTs used, Co shows a moderate activity and low selectivity towards COL, and HCAL is the major product ( $\approx 60\%$ ) followed by HCOL ( $\approx 30\%$ ).

The higher TOF obtained at a high filling yield could be correlated to the smaller NP<sub>in</sub> size compared to the NP<sub>out</sub> size. Another explanation could arise from the enrichment of reactants inside the CNT channels. Molecules such as H<sub>2</sub>, alkanes, alkenes, and carbon tetrachloride have been reported to bind more strongly on the interior surface of CNTs.<sup>[41]</sup> By combining first principles calculations with Monte Carlo simulation, Bao et al. have shown that both CO and H<sub>2</sub> molecules are enriched in a pressure range of 1–9 MPa inside single-walled CNT (SWCNT) channels.<sup>[3a]</sup> As positive orders are generally reported both for H<sub>2</sub> and cinnamaldehyde in the kinetic law of this reaction, the enrichment of these two reactants inside the CNT channels should induce a higher TOF. This latter effect could also induce differences in selectivity. These results highlight the possible role of too often unidentified/neglected confinement effects on the catalytic results obtained with CNT-supported metal NPs.

#### Conclusions

The preparation of metal catalysts supported on carbon nanotubes (CNTs) often involves a CNT purification/functionalization step with nitric acid. In most reports, the issue of nanoparticle (NP) location (exohedral vs. endohedral grafting) is ignored. In this study, we investigated the effects of many parameters, which included CNT pretreatment and diameter, the nature of the metal, the nature of the metal precursor, and the nature of the solvent on the metal NP location. The results obtained for Ru, Pd, PdRu, and Co NPs have shown that three factors should be taken into consideration to achieve high filling yields: 1) the opening of the CNT inner cavity that can be achieved by nitric acid oxidation, but other treatments are also efficient such as air<sup>[42]</sup> or CO<sub>2</sub><sup>[43]</sup> oxidation and treatment with steam<sup>[44]</sup> or sulfuric acid/potassium permanganate,<sup>[45]</sup> 2) the appropriate choice of solvent(s) in terms of viscosity but mainly surface tension, and 3) molecular surface recognition, as the metal precursor should present a higher affinity for the perfect inner surface than the outer, often defective one. This latter point is by far the most difficult to optimize as it involves complex chemistry between the carbon surface and coordination compounds. We have shown that the control of these factors can allow modulation of the filling yield of metal NPs between 10 and 80%. We have also shown the impact of the confinement of the active phase on the activity and selectivity of the produced catalysts for cinnamaldehyde hydrogenation. Thus, we hope that this study will prompt researchers who study CNT-supported metal catalysts to integrate the possibility of confinement effects to rationalize the catalytic results. Indeed, even if a few studies have reported that the confinement effect is not helpful for all reactions, and CNT-supported catalysts do not improve the activity for all reactions,<sup>[46]</sup> in many cases it does.

#### **Experimental Section**

#### **Catalyst preparation**

#### **MWCNTs** treatment

Small-diameter MWCNTs produced by catalytic chemical vapor deposition were supplied by Nanocyl, Belgium (purity of as-received CNTs above 95 wt%). Large-diameter CNTs (Pyrograph III) were supplied by Applied Sciences. Their specific surface area, measured by N<sub>2</sub> adsorption at liquid N<sub>2</sub> temperature, was  $38 \text{ m}^2 \text{g}^{-1}$ . Their average outer diameter is 120–150 nm, and their average inner diameter 50–70 nm. The as-received CNTs were treated with a 1:1 mixture of concentrated H<sub>2</sub>SO<sub>4</sub>/water at 140 °C for 3 h to remove amorphous carbon and residual metal catalyst. In our study, purified Nanocyl CNTs (2 g, **CNT0**) were suspended in concentrated nitric acid (80 mL, 65%) and heated to reflux at 140 °C for 3 h. After cooling, the CNTs were collected by filtration, washed with distilled water until neutralization of the filtrate (pH  $\approx$  6), and dried in air at 110 °C for 2 d to obtain **CNT1**. In addition, **CNT0** was ball-milled for 78 h in a Pulverisette 0 Fritsch apparatus

to obtain **CNT2**. Samples **CNT1HT** and **CNT2HT** were prepared by secondary heat treatment of **CNT1** under Ar and **CNT2** under Ar/ $H_2$  (10%  $H_2$  v/v), respectively, at 900°C for 2 h. The as-received Pyrograph III CNTs were oxidized by concentrated nitric acid (65%) at reflux for 3 h to produce **CNT3**. **CNT3** (1 g) was further refluxed in a solution of thionyl chloride (30 mL) for 24 h at 70°C under Ar, then the solvent was evaporated under vacuum and the CNTs were dried under vacuum for 24 h. Chlorinated CNTs (1 g) were reacted with hexadecylamine (HDA, 1 g) in THF (40 mL) at 65°C for 24 h. Finally, THF was evaporated and the CNTs were washed with ethanol (100 mL) to remove excess amine, and dried at 110°C for 24 h under vacuum to obtain **CNT4**.

#### Preparation of metal-filled CNTs

Different metallic precursors were used and dissolved in appropriate solvents, depending on their solubility, with a concentration calculated as to give a theoretical value of 5 wt% metal/CNT catalysts after the impregnation step:  $[Ru(NO)(NO_3)_3]$  (**Ru1**),  $[Ru_3(CO)_{12}]$ (**Ru2**), [Ru(COD)(COT)] (**Ru4**),  $Co(NO_3)_2$ ·6H<sub>2</sub>O (**Co1**), and Pd(NO\_3)\_2-(H<sub>2</sub>O)<sub>2</sub> (**Pd1**) in acetone, RuCl<sub>3</sub> (**Ru3**) in isopropanol, and  $[Pd_2(dba)_3]$ (**Pd2**) in toluene. CNTs (200 mg) were dispersed in a 20 mL solution of the metallic precursor in the suitable solvent by ultrasonication for 60 min. After ultrasonic treatment the mixture was stirred at RT for 12 h and then filtered. For **Ru1**, **Ru2**, **Ru3**, **Co1**, and **Pd1** precursors, the solids were dried at 110 °C for 24 h and then reduced at 300 °C for 2 h in a furnace under flowing H<sub>2</sub>/Ar (10% H<sub>2</sub> v/v). For **Pd2**, the solid was dried under vacuum and then reduced at RT overnight in a batch autoclave under 3–5 bar of H<sub>2</sub>.

#### **Catalyst characterization**

TEM was performed by using a JEOL JEM-1011 microscope coupled with an energy dispersive X-ray spectrometer (EDS), using accelerating voltages of 100 kV. The samples were dispersed by sonication in ethanol, then deposited on a holey carbon TEM grid and dried. TGA in air was conducted by using a Setaram apparatus using a temperature program of 25-1000°C with a heating rate of 10°C min<sup>-1</sup>. The specific surface area, pore volume, and pore size were measured by N<sub>2</sub> physisorption at  $P/P_0 = 0.99$  at liquid nitrogen temperature by using a Belsorpmini (BEL Japan Inc.) apparatus. The specific surface area was calculated according to BET theory, and the pore size and the pore volume were calculated by the Barrett-Joyner-Halenda (BJH) method based on the desorption branch of the isotherm. Raman spectra were recorded by using a Labram HR800 of Jobin Yvon Raman spectrometer (excitation wavelength = 632.82 nm). TPD profiles of CO and CO<sub>2</sub> were obtained by using an AMI-200 (Altamira Instruments) apparatus. In a typical experiment, the sample (100 mg) was subjected to a 5 °C min<sup>-1</sup> linear temperature rise up to 1100 °C under a He flow of 25 sccm. The amounts of CO (m/z=28) and CO<sub>2</sub> (m/z=44) desorbed from the samples were monitored with a mass spectrometer (Dymaxion 200 amu, Ametek).

#### Cinnamaldehyde hydrogenation

The reactions were performed in a stirred (900 rpm) autoclave (Top Industrie) under 20 bar of  $H_2$  at 100 °C for 3 h. A solution of CAL (2 g) in dioxane (40 mL) and catalyst (0.1 g) were transferred to the reactor. The mixture was purged five times with  $H_2$ . At 100 °C, the system was pressurized under 20 bar of  $H_2$ . The variation of  $H_2$  pressure was monitored and the liquid phase was analyzed by GC.

The selectivity and the conversion were calculated after 3 h of reaction based on GC analysis.

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