

## **Carbon nanotube-supported gold nanoparticles as efficient catalyst for the selective hydrogenation of nitroaromatic derivatives to anilines**

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### **Abstract**

Gold nanoparticles (AuNPs) with sizes between 3 and 10 nm were firmly supported on pristine multi-walled carbon nanotubes (MWCNT) in high yields by a facile linker-free deposition route using aqueous suspensions of pre-reduced gold precursors. For the first time, the resulting AuNP-MWCNT hybrid material was employed as catalyst for the hydrogenation of a series of substituted nitroarenes under mild reaction conditions. High catalytic activity with turnover frequencies (TOF) values up to 1200 h<sup>-1</sup> were achieved accompanied by a remarkable chemoselectivity. Recyclability tests did neither reveal leaching nor changes in size or oxidation states of the AuNPs. The concomitant presence of Au<sup>0</sup> and Au<sup>I</sup> accounts for both the superior catalytic performance and the high stability of the hybrid material. Preferential orientation of nitroarenes on the MWCNT surface due to  $\pi$ - $\pi$  interactions coupled with coulombic contact of the nitro group to the AuNPs most likely explains the high chemoselectivity of the hybrid material, and further underlines the valuable role of MWCNTs for catalytic reactions.

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## 1.- Introduction

Carbon nanotubes with their high surface area, high chemical stability, unique electronic properties and mechanical robustness provide an ideal support for the effective deposition of catalytically active metal nanoparticles such as Pt, Pd, Ru, Ag, or Au [1, 2]. Since the pioneering discovery of Haruta that gold in the form of nanoparticles can promote catalytic reactions [3], the field of gold catalysis has become a discipline of increasing interest. Today, several key synthetic transformations such as oxidation and hydrogenation reactions, among others, have been successfully developed [4-14]. AuNPs with sizes up to a few nanometers, including even subnanometric gold species, are considered critical to achieve high catalytic activity [15-17]. Moreover, the catalytic performance of the AuNPs also crucially depends on the support selection. For instance the hydrogenation of nitroarenes with AuNPs supported on oxides such as TiO<sub>2</sub> or Fe<sub>2</sub>O<sub>3</sub>, so-called “active supports”, proceeds with outstanding chemoselectivity when the nitro group coexists with other functional groups [18]. Here the different interactions of the nitro-containing reactants with both the AuNPs and the support but as well the proper AuNP-support interaction play an important role for the final outcome of the reactions [19, 20]. However, in order to obtain efficient catalytic activities the reactions usually have to be carried out under harsh reactions conditions, i.e. high hydrogen pressure and high temperature to compensate for otherwise low conversion rates [21-23]. Currently, the “active” supports are widely accepted as essential component for attaining high activity and chemoselectivity. Consequently, “inert” supports, such as SiO<sub>2</sub> and carbon materials yet have aroused very limited

interest. In particular, studies on the use of AuNP-CNT hybrid materials for the hydrogenation of nitroaromatic derivatives are still in its infancy [24]. Moreover, to the best of our knowledge, AuNPs hybrid materials comprised of a directly accessible non-coated CNT surface, suitable to elucidate the influence of this “inert” support, have never been employed in these types of technologically relevant catalytic reactions.

Recently, we have reported on the firm attachment of well-dispersed palladium nanoparticles (PdNPs) on multi-walled carbon nanotubes (MWCNTs) by employing facile linker-free methods [25-27]. The corresponding hybrid material revealed high catalytic activity in Heck and Suzuki C-C coupling reactions, as well as high selectivity in the hydrogenation of different alkenes under very mild conditions. The strong interactions between the PdNPs and the MWCNTs support even favored the reuse of the catalyst. These encouraging findings, which profit from a directly accessible CNT surface obtained through linker-free synthesis protocols, offer promise for the preparation of analogous AuNP-CNT hybrid materials and their use as catalyst in hydrogenation reactions of nitroarenes.

In this work we first will show that a linker-free method can be used to prepare a AuNP-MWCNT hybrid material consisting of AuNPs with sizes between 3 and 10 nm firmly supported on the surface of non-modified pristine MWCNTs. This facile, fast and up-scalable preparation method is based on the electrostatic deposition of pre-reduced gold precursors in aqueous solutions onto pristine MWCNTs. Subsequently, we will demonstrate for the first time that the developed AuNP-MWCNT hybrid material with its freely accessible MWCNT surface can be employed as efficient catalyst for the hydrogenation of a series of substituted nitroarenes under mild conditions. Its high activity and chemoselectivity is comparable to AuNPs supported on commonly used metal oxide supports. Finally, by thoroughly characterizing the catalyst before and after

the catalytic reactions, we not only will prove its high chemical stability and value for its reuse but also suggest a model explaining the favorable interactions involved in the hydrogenation process and the important role of carbon nanotubes as support material in this catalytic reaction.

## **2. Experimental**

### *2.1. Materials*

MWCNTs were obtained from Nanocyl Co, Belgium (Nanocyl<sup>TM</sup> NC7000, 90% carbon purity) and used without further treatment. The reagents for the synthesis of the composites such as chloroauric acid (HAuCl<sub>4</sub>), trisodium citrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>) and sodium borohydride (NaBH<sub>4</sub>), as well as all nitro compounds for the catalytic experiments, were purchased from various commercial sources and used as received.

### *2.2. Synthesis of the Au-NP/MWCNT hybrid material*

A solution of HAuCl<sub>4</sub> in water ( $5 \times 10^{-4}$  M, 10 mL) was prepared at room temperature in a round bottom flask. A solution of trisodium citrate in water ( $5 \times 10^{-4}$  M, 10 mL) was added, followed by the dropwise addition of a freshly prepared cold (0 °C) solution of sodium borohydride in water (0.1 M, 0.6 mL) resulting in a red colored solution. Next, 100 mg of MWCNTs were dispersed in the solution under stirring during 60 minutes at room temperature until complete loss of the red color was observed. The dispersion was vacuum-filtered through a polycarbonate membrane of 0.3 μm pore size, washed with 300 mL of distilled water and dried in an oven at 100 °C during 24 hours yielding powderous Au-NP/MWCNT hybrid material. Larger amounts were synthesized by up-scaling the procedure by a factor of ten employing 100 mL of each solution and 1000 mg of MWCNTs.

### *2.3. General conditions for the catalytic hydrogenation of nitroarenes to anilines*

A water/ethanol mixture (50:50 v/v) of 10 mL containing the nitroarene derivative (0.5 mmol) and the AuNP-MWCNT hybrid material was prepared. Depending on the nature of the nitroarene substrate, the amount of AuNP-MWCNT was adjusted in order to achieve final Au catalyst/substrate ratios between 0.3 and 0.6 mmol %. A freshly prepared solution of NaBH<sub>4</sub> (60 mg, 1.6 mmol) in H<sub>2</sub>O (2 mL) was added dropwise to initiate the hydrogenation reaction. Stirring either at room temperature or 90 °C completed the reaction within a given time varying from 15 minutes to 7 hours. For each nitroarene substrate, the conditions employed (Au catalyst to substrate ratios, temperatures and reaction times) are detailed in section 3.2. Next, the resulting mixture was centrifuged. The solution was decanted with a pipette and basified with KOH (2 mL, 1.0 M solution). The organic product was extracted with CHCl<sub>3</sub> (2×20mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. The solvent was evaporated to dryness affording the corresponding aniline as a yellowish material. The AuNPs/MWCNTs material recovered from the centrifuged mixture was washed with water (50 mL), dried in an oven during 24 hours at 100 °C, and used in the next run in recyclability tests performed for the hydrogenation reaction of p-nitrobenzylalcohol under the same conditions.

### *2.4. Characterization*

UV-Vis absorption spectra of the AuNP-MWCNT dispersions were recorded at different reaction times in a Shimadzu spectrophotometer using a 1 cm quartz cuvette. The Au content in the AuNP-MWCNTs material was determined by Inductive Coupled Plasma Spectroscopy (ICPS) using a Jobin-Yvon 2000 Ultrace Analyzer. Powder X-ray diffraction (XRD) measurements were carried out at room temperature on a Bruker D8 Advance diffractometer using a Cu K<sub>α</sub> X-ray radiation. Size and distribution of AuNPs were studied by transmission electron microscopy (TEM) using a JEOL-2000 FXII

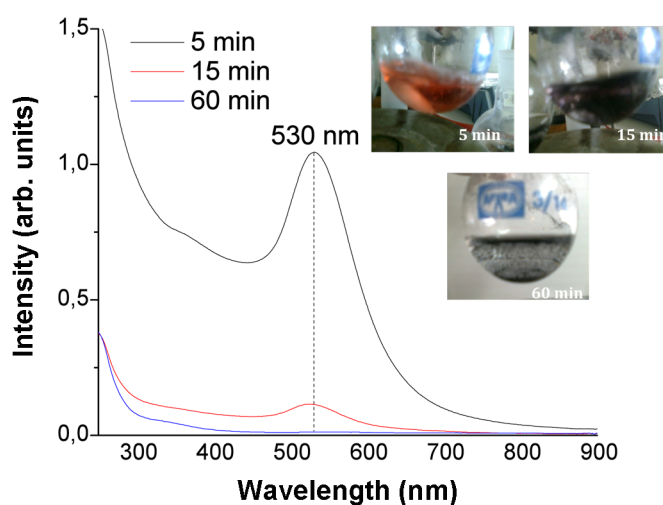
equipment working at 200 kV. Samples were dispersed in ethanol in an ultrasound bath for 10 min, and a drop of the solution containing the nanoparticles was placed onto a copper grid coated with carbon film. X-ray photoelectron spectroscopy (XPS) was carried out on an ESCAPlus Omicron spectrometer using a monochromatized Mg X-ray source (1253.6 eV). Data were analyzed using Casa XPS software package. The products of the catalytic reactions were characterized by infrared spectroscopy using a Perkin-Elmer Spectrum One spectrophotometer in the range from 4000 - 200  $\text{cm}^{-1}$ , and by nuclear magnetic resonance (NMR) spectroscopy on a Bruker Avance-400 spectrometer ( $\delta$ , ppm; J, Hz). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra in a  $\text{CDCl}_3$  solution at 25  $^\circ\text{C}$  were referenced using the solvent signal as internal standard. IR and NMR data were compared with those reported in the bibliography.

### **3. Results and Discussion**

#### *3.1. Synthesis of the AuNP-MWCNT hybrid material*

Gaining control on the size and loading of metal nanoparticles, as well as on the interactions between the metal and the carbon support, is key for the development of AuNP-MWCNT hybrid materials offering high catalytic activity through the supported gold nanoparticles. An efficient way to synthesize AuNP-carbon hybrid materials is the preparation of colloidal solutions of AuNPs and its adsorption onto the respective carbon material [6, 28, 29]. With the aim to obtain an AuNP-MWCNT hybrid material consisting of AuNPs directly anchored on a non-coated MWCNT surface freely accessible for catalytic reactions, we employed a very simple yet highly efficient linker-free synthesis approach. This is based on the the preparation of pre-reduced gold precursors in aqueous solutions, according to a combination of methods reported by Turkevich [30] and Brust [31], followed by their subsequent deposition on non-

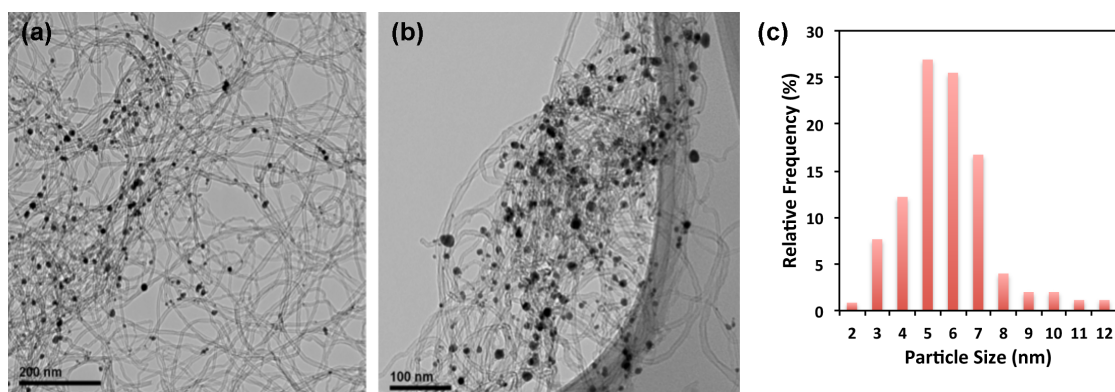
modified MWNTs. Briefly,  $\text{HAuCl}_4$  was reduced with  $\text{NaBH}_4$  in the presence of sodium citrate in a single-phase aqueous solution at ambient conditions. Sodium citrate acted as stabilizer [32] and the main reducing agent was  $\text{NaBH}_4$  providing fast reduction and nucleation conditions. The formation of gold nanoparticles was indicated by an intense red color. Addition of the pristine MWCNTs gradually turns the red-colored suspension clear, thus suggesting the deposition of AuNPs. Upon simple stirring, and without the need for stabilizing additives and long sonication times as formerly reported by Shi [33], our straightforwardly improved process concluded within a significantly reduced reaction time of 1 h only, as revealed by UV-vis spectroscopy of supernatant aliquots taken at different reaction times (Fig. 1).



**Fig. 1 - UV-Vis spectra at different times of the synthesis of AuNP-MWCNT hybrid material. Inset shows corresponding photos of the colloidal dispersion.**

The UV-Vis spectrum of the AuNPs dispersion exhibited the characteristic surface plasmon resonance peak (SPR) at 530 nm whose position depends on the size and shape of the gold nanoparticles [34]. This peak was still visible after 5 minutes of reaction time, thus revealing that most of the gold nanoparticle species were still well stabilized in the suspension. After 15 minutes of reaction time the intensity of the SPR peak

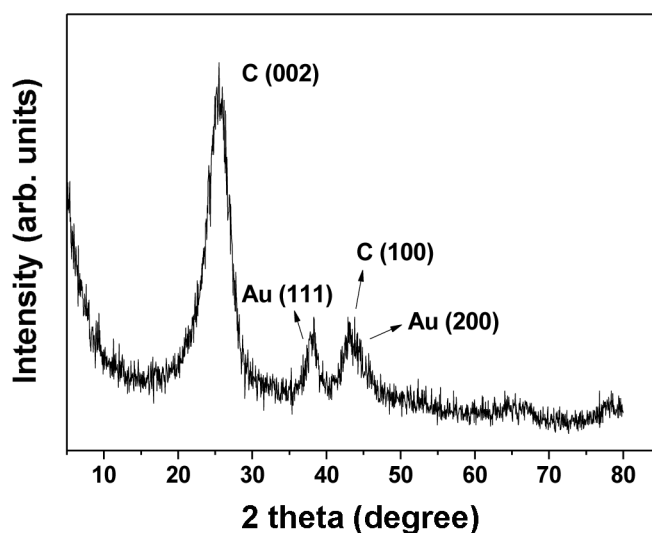
notably decreased, suggesting that the gold nanoparticles were deposited onto the carbon surface. Interestingly, the position of the SPR band did not shift during the deposition. This proves the absence of alterations in the size or shape of the AuNPs and once more underlines their high degree of stabilization. After barely 60 minutes, the absorption completely disappeared, evidencing that AuNPs were effectively deposited onto the carbon surface. The thus obtained AuNP-MWCNT material was washed and dried. ICPS analysis revealed an average gold loading on the nanotube of 0.85 wt. %, which represents an averaged deposition yield of 85 %. Indeed, a really minor amount of gold (0.07 mg/L) was detected in the washing water by ICPS analysis, evidencing a firm anchoring of the AuNPs to the MWCNT surface. No change in the deposition yield was observed for the AuNP-MWCNT material synthesized under up-scaled conditions. TEM images of the AuNP-MWCNT material show AuNPs homogeneously dispersed on the non-modified MWCNT surfaces (Fig. 2 a, b) with particle sizes ranging from 3 to 10 nm with a maximum population at about 5 to 6 nm as obtained from a statistical base of 400 particles (Fig. 2c). Most likely, the range of the AuNPs sizes in our work is a consequence of both, the rapid reduction process and the low amount of gold employed. This facilitates their stabilization and considerably reduces the tendency for agglomeration on the MWCNT surface.



**Fig. 2 – (a, b) TEM images of the AuNP-MWCNT hybrid material. (c) Size distribution of the deposited AuNPs.**

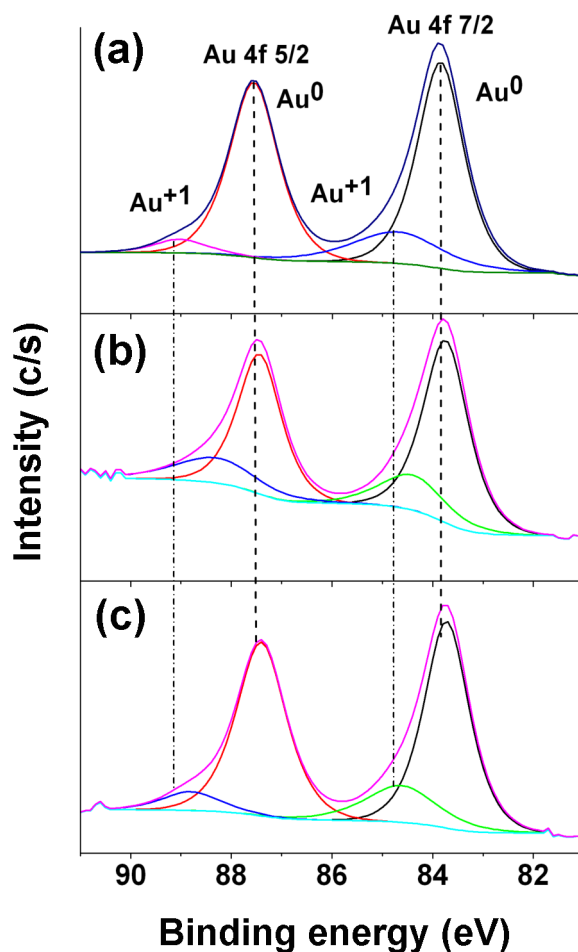


The X-Ray powder diffractogram of the AuNP-MWCNT material (Figure 3) revealed typical peaks of MWCNTs at two-theta values of 26° and 44° belonging to the (002) and (100) carbon planes. The additional peak at 38°, corresponding to the Au (111) diffraction plane, clearly indicated the existence, and thus the successful deposition of AuNPs on the MWCNTs. The fact that the Au (200) peak was only observable as a weak shoulder at 44.2° and higher-order Au peaks were not seen is indicative for both, the low amount of AuNPs, but also the small particle size, leading to broad line shapes and very low intensities. Scherrer analysis revealed an average crystallite size of 4.5 nm, in agreement with the TEM observations.



**Fig. 3 – X-ray powder diffractogram of the AuNP-MWCNT hybrid material.**

The oxidation state of the deposited AuNPs, a critical factor for catalytic reactions was elucidated by XPS studies on freshly prepared AuNP-MWCNT material and after its use as catalyst. Representative XPS spectra are shown in Figure 4. For all cases, two characteristic bands, corresponding to the  $4f_{5/2}$  and  $4f_{7/2}$  atomic orbitals, were observed.



**Fig. 4 - XPS spectra of Au 4f<sub>5/2</sub> and Au 4f<sub>7/2</sub> orbitals of the AuNP-MWCNT hybrid material. (a) freshly prepared, and (b, c) recovered after the hydrogenation of o-nitrophenylalcohol and 2-nitro-5-tiophencarboxaldehyde, respectively.**

After deconvolution of these bands two main peaks at 87.4 and 83.7 eV, assigned to Au<sup>0</sup>, and two less intense peaks at 88.6 and 84.7 eV corresponding to Au<sup>I</sup>, were observed [35]. A contribution of 78 at. % for Au<sup>0</sup> vs 22 at. % for the Au<sup>I</sup> species was calculated from the integrated areas. The existence of a non negligible amount of Au<sup>I</sup> in the composition of the nanoparticles might have remarkable consequences for their stabilization on the surface of MWCNTs and for their catalytic activity, which strongly depends on the metal-support interaction [4, 19, 20, 23]. First of all, the presence of the two oxidation states is in well-agreement with the growth model of AuNPs in aqueous solutions proposed by Liz-Marzán [36]. Here it is suggested that the synthesis of AuNPs

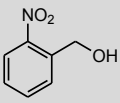
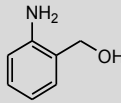
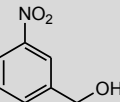
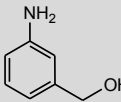
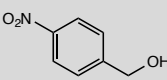
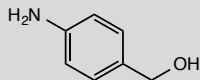
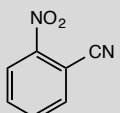
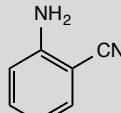
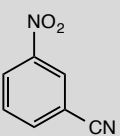
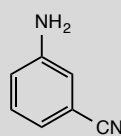
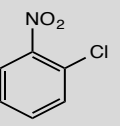
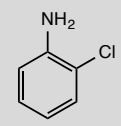
by citrate reduction of Au<sup>III</sup> complexes occurs in two well-defined steps. In the first one, a fast oxidation from Au<sup>III</sup> to Au<sup>I</sup> is taking place, while in the second further oxidation to Au<sup>0</sup> proceeds at a considerably slower rate. Once the gold nuclei are formed, both Au<sup>III</sup> and Au<sup>I</sup> co-exist in the solution during the growth process. The addition of borohydride ions to the reaction during the actual growth stages results in fresh formation of small gold nuclei in solution and the instant peptization of the existing aggregates. Disproportionation of Au<sup>I</sup> controls the rate of particle growth and the initial number of primary nuclei. This results in the concomitant contribution of a minor Au<sup>I</sup> and major Au<sup>0</sup> phase to the overall composition of the AuNPs, which are stabilized in the solution through complexation of the carboxylate groups of the citrate anions [32]. Second, in aqueous solution, the positively charged AuNPs and the anionogenic carboxylic groups intrinsically present on the MWCNTs establish an adsorption process driven by long-range electrostatic forces [29]. The minor Au<sup>I</sup> phase of the deposited AuNPs, which is in close contact with the negatively charged MWCNT surface, thus becomes responsible for the strong non-covalent interaction between the overall AuNPs and the MWCNTs. Consequently, the major part of the freely available AuNP surface relates to the Au<sup>0</sup> phase and would be largely available for catalytic reactions. Profiting from this unique situation, we subsequently tested the synthesized AuNP-MWCNTs material for the first time as catalyst in hydrogenation reactions of different types of nitroarenes and nitroheteroarene compounds.

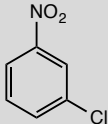
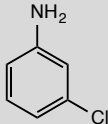
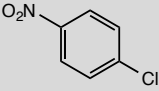
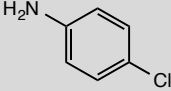
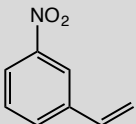
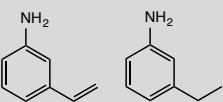
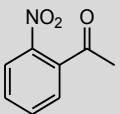
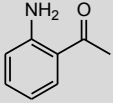
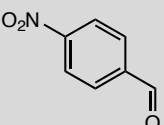
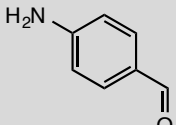
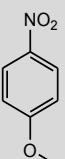
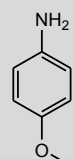
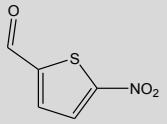
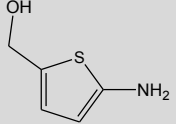
### *3.2. Catalytic activity of the AuNP/MWCNT hybrid material in hydrogenation reactions of nitroaromatic compounds*

The catalytic hydrogenation of nitroaromatic derivatives was performed using low amounts of catalyst (typically between 0.3-0.6 mmol %) in a mixture EtOH/water as solvent. NaBH<sub>4</sub> was chosen as reducing agent due to the extreme simplicity of the

work-up. It allows the reactions being carried under very mild conditions (25-90 °C, ambient pressure) and avoids the use of dangerous and expensive high-pressure reactors employing hydrogen gas at elevated temperatures. The most representative results are presented in Table 1. A control experiment in the absence of both gold and MWCNTs using *p*-nitrobenzylalcohol at room temperature showed a low conversion of 9% only. An additional control experiment with only MWCNTs did not reveal catalytic properties, which also is in agreement with our recent findings on reduced graphene oxide [27].

**Table 1 – Reduction of nitroarenes using the AuNP/MWCNT catalyst.**

Entry	Substrate	Catalyst (%) <sup>a</sup> Time (h)	T (°C)	Product	Yield (%) <sup>b</sup>	TOF (h <sup>-1</sup> ) <sup>c</sup>
1		0.3	90		80	1067
		0.25				
2		0.3	90		85	1133
		0.25				
3		0.3	25		90	1200
		0.25				
4		0.3	90		95	79
		4				
5		0.3	90		95	79
		4				
6		0.3	90		94	78
		4				

7		0.3 4	90		97	81
8		0.3 4	90		98	82
9		0.3 4	90		86/14 <sup>d</sup>	-
10		0.3 4	90		95	79
11		0.3 4	25		61	51
12		0.6 7	25		100	24
13		0.5 5	25		62	25

<sup>a</sup> Catalyst (%) = [(mmol Au)/(mmol substrate)]×100.  
<sup>b</sup> isolated yield.  
<sup>c</sup> TOF = [mmol product/(mmol Au×time(h))].  
<sup>d</sup> full conversion, molar ratio of the mixture determined by NMR.

The hydrogenation of nitrobenzylalcohol, *ortho*- (*o*-), *meta*- (*m*-), and *para*- (*p*-) isomers, took place with outstanding chemoselectivity. The alcohol group was not modified (entries 1-3) and only the selective transformation of the nitro group into an amine was observed. Moreover, a complete conversion was achieved in less than 15 minutes, and the corresponding *o*-, *m*-, and *p*-aminobenzylalcohols were obtained in

very good yields after a very simple workup. Additionally, it is important to mention that other products derived from partial hydrogenation or side-coupling reactions (hydroxylamines, azoxybenzene, azobenzene) were not observed. This explains the high TOF values in the range of 1000-1200 h<sup>-1</sup>, which notably improve the best data yet obtained for other gold-supported catalysts in this type of reactions [37-41]. Although these recent reports reveal good yields the reaction times with values between 2.5 h and 24 h are significantly higher, therefore affording TOF values in the range 12-40 h<sup>-1</sup>. A comparison of best values found in the literature is presented in Table 2. It should be kept in mind that comparative data are not available for carbon supported AuNPs for this type of reaction and thus have to refer to metal-oxide supported AuNPs (Table 2).

Prompted by these remarkable results, we used our catalyst for the hydrogenation of more challenging substrates such as nitroarenes bearing other easily reducible moieties like *o*- and *m*-nitrobenzotrile (entries 4 and 5), all isomers (*o*-, *m*- and *p*-) of chloronitrobenzene (entries 6-8) and *m*-nitrostyrene (entry 9). We found full chemoselectivity for the reduction of the nitro group in presence of the cyano moiety (entries 4 and 5), therefore *o*- and *m*-aminobenzotrile can be obtained in very good yields (around 95%), without detection of other hydrogenated products, although the reaction time was longer than in the case of the nitrobenzylalcohols (4h vs. 15 min). However, even using longer reaction times the obtained results in terms of yield of isolated product and selectivity are similar or even improve those obtained by other authors [37] (see Table 2 and Table S1 in Supporting Information). Apparently, our AuNP-MWCNT catalyst provides an optimum ratio between yield and selectivity of the final product, while easy to handle at the same time.

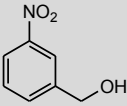
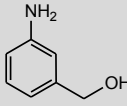
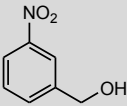
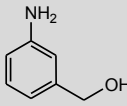
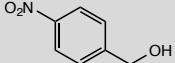
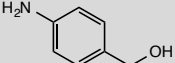
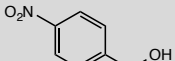
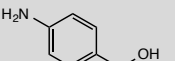
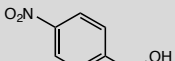
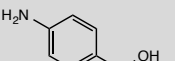
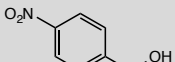
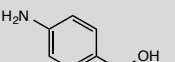
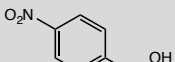
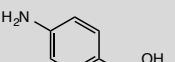
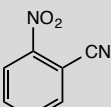
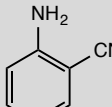
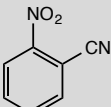
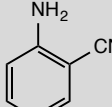
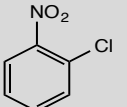
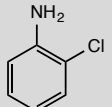
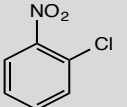
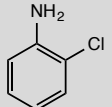
The results obtained in the hydrogenation of the different isomers of chloronitrobenzene (entries 6-8, Table 1) point in the same direction. In all cases complete conversions were observed and the corresponding chloroanilines were isolated in very good yields (94-98 %), showing that the hydrogenation takes place with total chemoselectivity. This outstanding observation also implies the absence of dehalogenation processes commonly found for other types of metal catalysts, and thus underlines the benefits of our catalytic system to avoid this undesired problem. Curiously, we have not observed differences in the optimized reaction conditions for each isomer, as it has been recently reported [38]. Once again, the comparison with other catalysts containing supported Au on TiO<sub>2</sub> or SiO<sub>2</sub> (Table 2) clearly reveals higher TOF values for our system [38, 41, 42]. Only one case shows slightly higher values, however, on cost of the use of a high pressure of CO [39]. The case of *m*-nitrostyrene (entry 9) is slightly different, since under the same reaction conditions (0.3% Au, 90 °C, 4h) we observed a 86% of *m*-vinylaniline together with a 14% of *m*-ethylaniline, indicating an over-reduction of the double bond. Attempts to reduce the amount of the ethylaniline by-product changing the reaction time and/or the temperature were not successful yet.

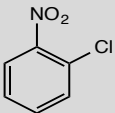
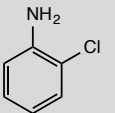
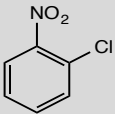
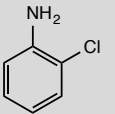
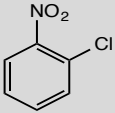
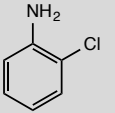
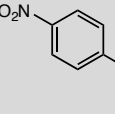
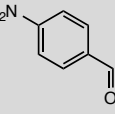
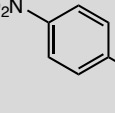
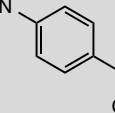
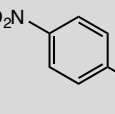
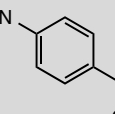
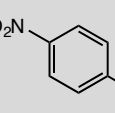
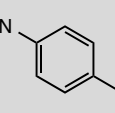
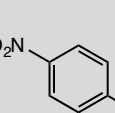
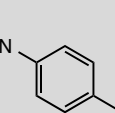
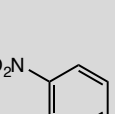
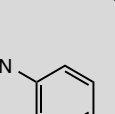
The competitive hydrogenation of the nitro moiety with other coexisting functional groups was further examined. The hydrogenation of *o*-nitroacetophenone afforded the corresponding *o*-aminoketone with good yield (95%) (entry 10) and excellent chemoselectivity, under the same conditions employed in the preceding cases. Similarly, 4 hours of reaction time were required to complete conversion of *p*-nitrobenzaldehyde to *p*-aminobenzaldehyde (entry 11). These results are outstanding in terms of conversion and chemoselectivity, and are truly competitive with the best data recently published (see Table 2) [18, 21, 37, 39]. Our catalyst required somewhat similar or shorter reaction times (4 h vs. 3.5-12 h) to obtain best TOF values compared

with other systems and, in addition, we could employ milder reaction conditions (25 °C vs. 60-120 °C) and work at atmospheric pressure, thus avoiding the use of pressure reactors. Only the reactions reported by Corma et al. [18] are more efficient in shorter reaction times (Table 2). Moreover, in spite of the known reactivity of the keto function in aldehydes or ketones towards NaBH<sub>4</sub>, full chemoselectivity was observed [43]. To our delight, the gold catalyst also showed high efficiency for the reduction of industrially relevant substrates, scarcely analysed in the literature, such as p-nitroanisole (entry 12), which smoothly afforded the corresponding methoxyaniline at room temperature in quantitative yield, without detection of partially hydrogenated intermediates. Even more interestingly, heterocycles such as 5-nitro-2-thiophenecarboxaldehyde could be reduced, although not chemoselectively, to give (5-aminothiophen-2-yl)methanol (entry 13) in good yield without modification of the heterocyclic moiety. It is often encountered that nitro-substituted *N*- or *O*-heterocycles, such as nitrofuranes, nitroquinolines or nitropyrazoles can undergo clean hydrogenation of the nitro group affording the expected amino-heterocycles, even using gold catalysts [37-41]. However, when dealing with thiophene rings this reaction is seldomly used [44], and the synthesis of aminothiophenes is carried out by other methods [45-48]. This finding, although preliminary, paves the way to new synthetic pathways for the preparation of interesting intermediates such as aminothiophenes.



**Table 2 – Comparison of AuNPs catalytic activity on different support materials**

Substrate	Support	Product	Yield (%)	TOF (h <sup>-1</sup> )	Conditions	NPs Ø (nm)	Ref.
	TiO <sub>2</sub>		89	12	Au (0.8%), N <sub>2</sub> H <sub>4</sub> , 60 °C, 9 h	n. r.	[37]
	Pristine MWCNTs		85	1133	Au (0.3%) NaBH <sub>4</sub> , 90 °C, 0.25 h	3-10	this work
	TiO <sub>2</sub>		96	32	Au (1.0%), HCO <sub>2</sub> NH <sub>4</sub> , 25 °C, 3 h	1.5-3.5	[38]
	TiO <sub>2</sub>		99	39.6	Au (1.0%), CO (5 atm), 25 °C, 2.5 h	1.9	[39]
	Fe <sub>3</sub> O <sub>4</sub>		91	3.8	Au (1.0%), TMDS, 25 °C, 24 h	10±3.6	[40]
	TiO <sub>2</sub>		97	32.3	Au (1.0%), CO (5 atm), 25 °C, 3 h	n. r.	[41]
	Pristine MWCNTs		90	1200	Au (0.3%) NaBH <sub>4</sub> , 25 °C, 0.25 h	3-10	this work
	TiO <sub>2</sub>		92	9.6	Au (0.8%), N <sub>2</sub> H <sub>4</sub> , 60 °C, 12 h	n. r.	[37]
	Pristine MWCNTs		95	79	Au (0.3%) NaBH <sub>4</sub> , 90 °C, 4 h	3-10	this work
	TiO <sub>2</sub>		80	10	Au (1.0%), HCO <sub>2</sub> NH <sub>4</sub> , 25 °C, 8 h	1.5-3.5	[38]
	TiO <sub>2</sub>		99	123	Au (1.0%), CO (5 atm), 25 °C, 0.8 h	1.9	[39]

	SiO <sub>2</sub>		100 <sup>a</sup>	-	Au (0.16%), H <sub>2</sub> (4 MPa), 140 °C, 3 h	7-9	[42]
	TiO <sub>2</sub>		65	11	Au (1.0%), CO (5 atm), 25 °C, 6 h	n. r.	[41]
	Pristine MWCNTs		94	78	Au (0.3%) NaBH <sub>4</sub> , 90 °C, 4 h	3-10	this work
	TiO <sub>2</sub>		99.0 <sup>a</sup>	-	Au (1.14%), H <sub>2</sub> (10 bar), 100 °C, 1.25h		[18]
	Fe <sub>2</sub> O <sub>3</sub>		99.4 <sup>a</sup>	-	Au (4.30%), H <sub>2</sub> (10 bar), 100 °C, 1 h		[18]
	TiO <sub>2</sub>		90 <sup>b</sup>	9.4	Au (0.8%), N <sub>2</sub> H <sub>4</sub> , 60 °C, 12 h	n. r.	[37]
	TiO <sub>2</sub>		99	28.3	Au (1.0%), CO (5 atm), 25 °C, 3.5 h	1.9	[39]
	TiO <sub>2</sub>		99 <sup>a</sup>	82.5	Au (0.2%), H <sub>2</sub> (0.9 MPa), 120 °C, 6 h	n. r.	[21]
	Pristine MWCNTs		61	51	Au (0.3%) NaBH <sub>4</sub> , 25 °C, 4 h	3-10	this work

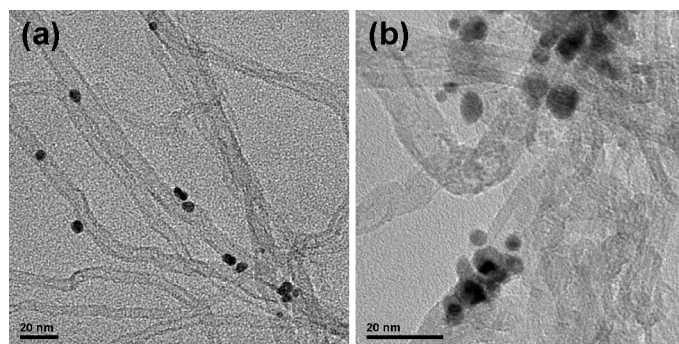
TMDS = tetramethyldisiloxane; n. r. = not reported

<sup>a</sup> conversion values; isolated yields were not reported, thus no TOF values can be calculated

<sup>b</sup> the obtained product is not the expected aminobenzaldehyde, but the product of further condensation of the aldehyde with hydrazine

### 3.3. Characterization of AuNP-MWCNT catalyst after the hydrogenation process and recyclability performance

To gain insight into possible leaching or agglomeration effects during the reduction, the AuNP-MWCNT catalyst was characterized after its successful use in several hydrogenations of *o*-nitrobenzylalcohol carried out under standard conditions (heating at 90 °C for 0.25h). ICP-AES analysis of the recovered catalyst did not provide any indication for leaching. This observation reveals a strong interaction between the AuNPs and the MWCNT support, which is not easily disrupted even under harsher conditions. We neither could detect any significant changes in size and morphology using TEM (Fig. 5), which further evidences the successful stabilization of the AuNPs on the MWCNT surface. Moreover, it underlines that a covalent linkage achieved through tedious treatment and functionalization steps of the carbon nanotubes [49-53] is not required to obtain a favourable interaction between the AuNPs and the MWCNTs.



**Fig. 5 - Representative TEM images of the AuNP/MWCNT hybrid material after the first catalytic run of *o*-nitrobenzylalcohol hydrogenation (Table 1, entry 1).**

The XPS analyses of the catalysts after the reaction (see Fig. 4b, c) revealed the same Au<sup>0</sup>/Au<sup>I</sup> ratio as the one of the freshly prepared material (Fig. 4a), suggesting that the composition of the AuNPs does not change through the catalytic cycle. Once again, the presence of gold atoms with partial positive charge apparently provides a clear

advantage for improving the stability of the hybrids via electrostatic interactions and contributes to simplifying notably the synthesis methodology. Moreover, the XPS data also suggested that the catalyst after the first run is ready to start a new cycle exactly under the same conditions than those prior to the first run. Table 2 resumes the yields obtained in five consecutive runs for the hydrogenation of *p*-nitrobenzylalcohol (entry 3), carried out with a 0.3% Au loading at room temperature. Indeed, the AuNP/MWCNT catalyst showed a good recyclability behaviour. The second run afforded a yield almost an identical to the first one. From the second to the the third run the yield decreased by 15 % but then remained constant for the subsequent runs. Thus, the catalyst kept a high activity during at least the five first catalytic runs without noticeable signs of deactivation.

Table 3 – Recyclability<sup>a</sup> of the AuNP/MWCNT catalyst.

Run	Yield (%)
1st	90
2nd	89
3rd	75
4th	75
5th	75

<sup>a</sup> Hydrogenation reaction of *p*-nitrobenzylalcohol.

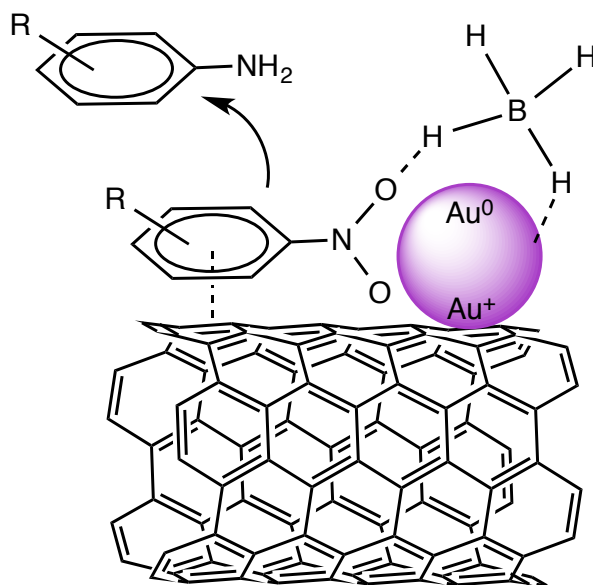
### 3.4 Mechanism of the catalytic reaction

High catalytic activity of supported AuNPs is considered to be intimately related to a critical range of particle sizes between 3 and 5 nm [4, 6, 54-56], but as well as to the support and favorable substrate-support interactions [2, 55]. Since the AuNPs attached

to the MWCNTs in our hybrid catalyst exhibit sizes between 3 and 10 nm with a mean value of about 5 to 6 nm it seems questionable that the high TOF values up to 1200 h<sup>-1</sup> and the outstanding chemoselectivity in our AuNP-MWCNT material were achieved only by the smallest AuNPs. It also should be born in mind that the supporting MWCNTs themselves are inactive and that both oxidation states of the AuNPs, i.e. Au<sup>0</sup> and Au<sup>I</sup> are catalytically relevant [18-21]. Thus favorable substrate-support interactions should be taken into account to explain the high catalytic activity of the AuNP-MWCNT material. Indeed, it is well known that nitroaromatic  $\pi$ - $\pi$  interactions with carbon nanotubes are stronger than those of other aromatic compound [57, 58]. The electron rich  $\pi$ -surface of the carbon nanotube can act as electron donor to a strong electron acceptor such as a nitroaromatic compound. Consequently, it is easy to envisage that the interaction of the MWCNT surface with the generated electron-rich aniline is considerably weaker than the one with the corresponding nitro precursor, at least taking into account only the  $\pi$ - $\pi$  interaction. This contributes to an easy removal of the weakly interacting aniline from the surface of the catalyst facilitating its replacement by another precursor molecule. In this way, undesired accumulations of products are avoided and fast processes and high catalytic activities are enabled.

Furthermore, the high chemoselectivity of our AuNP-MWCNT catalyst most likely also is a direct consequence of the favorable substrate-support interaction [19, 20, 23]. On one hand, the nitroarenes can establish a strong  $\pi$ - $\pi$  interaction with the MWCNT. On the other hand, additional interactions in the neighborhood of the metallic nanoparticle can be created, for instance between the negatively charged oxygen atoms of the nitro group and the cationic gold atoms present in the AuNP. Taking into account all these considerations we can propose a preferential approximation of the nitroarene to the AuNP, as illustrated in Figure 6. Here the aromatic ring establishes  $\pi$ - $\pi$  interactions with

the MWCNT surface while the nitro group points to the cationic gold in the AuNP. This preferred orientation of the nitro group, closer to the gold than to the other less polar functional groups, should be the responsible of the observed chemoselectivity. The catalytic cycle can be closed using the well-known interaction between gold and borohydride, studied in-depth due to their promising results in fuel cells [59], and the subsequent hydrogen transfer from the borohydride to the nitroarene [60]. All these steps likely occur at the surface of the AuNP, where it is assumed that the catalysis takes place [4, 6, 61-63]. However, it becomes also clear that the carbon nanotubes effectively influence in this type of processes contributing to the high TOF values and high chemoselectivity. Therefore, in contrast to the widely accepted assumption of their role as a merely “inert“ support, carbon nanotubes should be considered as "active" part of the catalyst system.



**Fig. 6 - Proposed interactions between the different components of the catalytic reaction.**

#### 4. Conclusions

AuNPs with sizes in the range of 3 to 10 nm have been firmly attached onto non-modified MWCNTs by a facile, rapid, and linker free synthesis method based on the

electrostatic deposition of reduced gold precursors from aqueous suspensions. The resulting AuNP-MWCNT hybrid material with its freely accessible MWCNT surface exhibits a high catalytic activity for the hydrogenation of substituted nitroarenes. This is expressed by TOF values as high as  $1200 \text{ h}^{-1}$  and outstanding chemoselectivity when alcohols, nitriles, olefins, halogens, ketones, aldehydes or ethers are present as additional functional groups. The AuNP-MWCNT catalyst is also efficient for the hydrogenation of heterocyclic rings such as nitrothiopne derivatives. These results outperform, or at least compete with existing data for comparable systems and reactions. Furthermore, absence of relevant leaching, lack of agglomeration and preservation of the oxidation states of the AuNPs upon the reuse of the AuNP-MWCNT catalyst underlines its remarkable recycling properties. This is a consequence of the strong gold-support interaction facilitated through the concomittant presence of two catalytically relevant oxidation states in the AuNP, namely  $\text{Au}^{\text{I}}$  and  $\text{Au}^{\text{0}}$ . However, the high catalytic activity could be inferred not only from the strong gold-support interaction, but also from favourable  $\pi$ - $\pi$  interaction between the nitroarenes and the MWCNTs. Allowing for a coulombic contact between the nitro group and the AuNP this enables a preferential orientation of the nitroarene, which accounts for the high chemoselectivity of the AuNP-MWCNT catalyt. These findings emphasize the valuable role of carbon nanotubes as catalyst support and thus provide further important insights to the wider field of gold catalysts.

### **Acknowledgements**

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**Carbon nanotube-supported gold nanoparticles as efficient catalyst for the  
selective hydrogenation of nitroaromatic derivatives to anilines**

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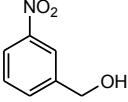
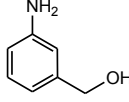
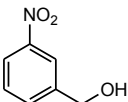
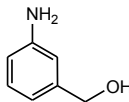
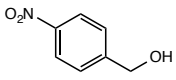
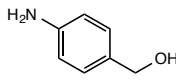
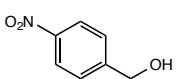
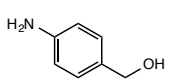
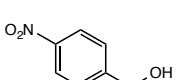
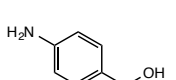
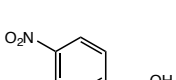
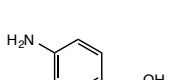
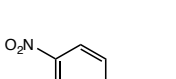
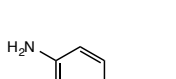
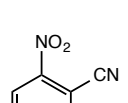
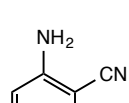
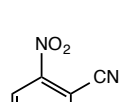
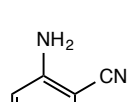
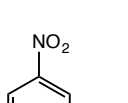
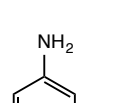
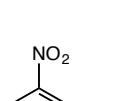
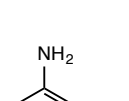
- Table S1: Comparison of AuNPs catalytic activity on different support materials
- References for Table S1

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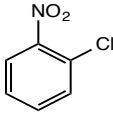
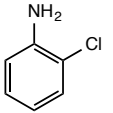
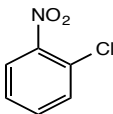
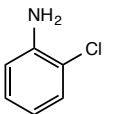
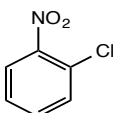
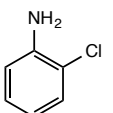
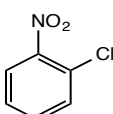
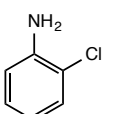
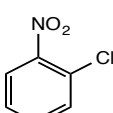
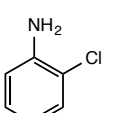
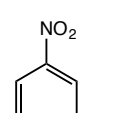
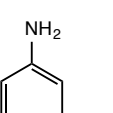
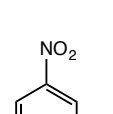
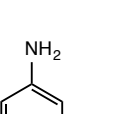
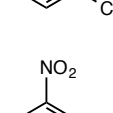
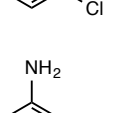
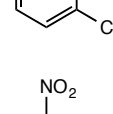
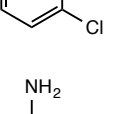
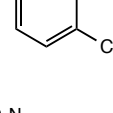
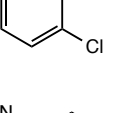
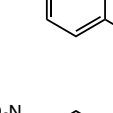
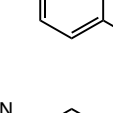
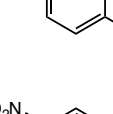
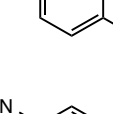
\* Corresponding authors. Tel: +34 976 73 39 77, E-mail: [wmaser@icb.csic.es](mailto:wmaser@icb.csic.es) (WMaser). Tel: +34 976 76-2302/-1187, E-mail: [esteban@unizar.es](mailto:esteban@unizar.es) (E.P. Urriolabeitia)

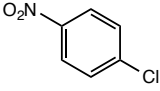
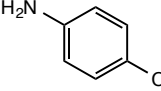
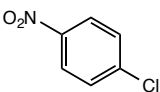
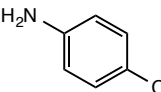
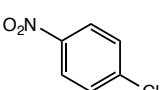
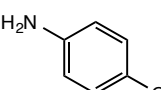
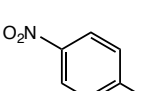
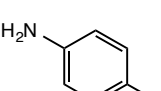
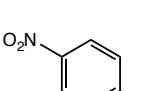
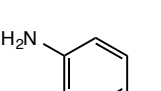
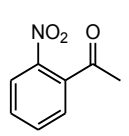
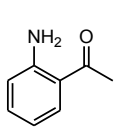
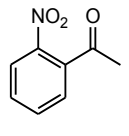
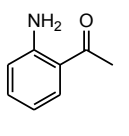
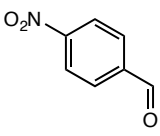
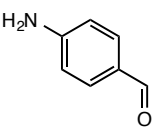
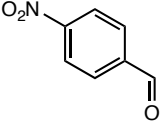
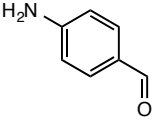
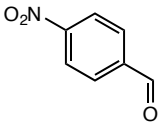
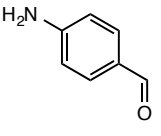
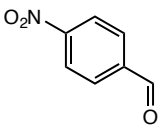
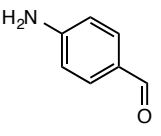
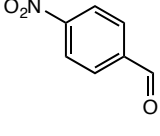
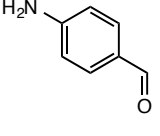
**Table S1**

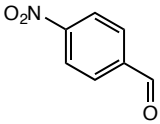
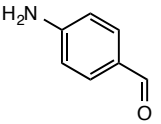
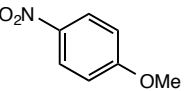
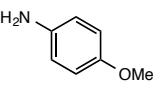
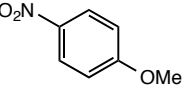
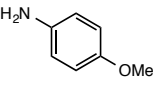
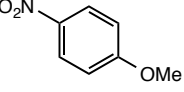
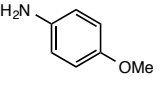
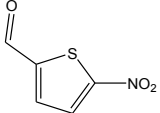
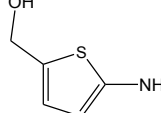
Comparison of AuNPs catalytic activity on different support materials

Substrate	Support	Product	Yield (%)	TOF (h <sup>-1</sup> )	Conditions	NPs $\varnothing$ (nm)	Ref.
	TiO <sub>2</sub>		89	12	Au (0.8%), N <sub>2</sub> H <sub>4</sub> , 60 °C, 9 h	n. r.	[1]
	Pristine MWCNTs		85	1133	Au (0.3%) NaBH <sub>4</sub> , 90 °C, 0.25 h	3-10	this work
	TiO <sub>2</sub>		96	32	Au (1.0%), HCO <sub>2</sub> NH <sub>4</sub> , 25 °C, 3 h	1.5-3.5	[2]
	TiO <sub>2</sub>		99	39.6	Au (1.0%), CO (5 atm), 25 °C, 2.5 h	1.9	[3]
	Fe <sub>3</sub> O <sub>4</sub>		91	3.8	Au (1.0%), TMDS, 25 °C, 24 h	10±3.6	[4]
	TiO <sub>2</sub>		97	32.3	Au (1.0%), CO (5 atm), 25 °C, 3 h	n. r.	[5]
	Pristine MWCNTs		90	1200	Au (0.3%) NaBH <sub>4</sub> , 25 °C, 0.25 h	3-10	this work
	TiO <sub>2</sub>		92	9.6	Au (0.8%), N <sub>2</sub> H <sub>4</sub> , 60 °C, 12 h	n. r.	[1]
	Pristine MWCNTs		95	79	Au (0.3%) NaBH <sub>4</sub> , 90 °C, 4 h	3-10	this work
	TiO <sub>2</sub>		88	587	Au (0.1%), NH <sub>3</sub> BH <sub>3</sub> , 25 °C, 1.5 h	n. r.	[6]
	Pristine MWCNTs		95	79	Au (0.3%) NaBH <sub>4</sub> , 90 °C, 4 h	3-10	this work



	TiO <sub>2</sub>		80	10	Au (1.0%), HCO <sub>2</sub> NH <sub>4</sub> , 25 °C, 8 h	1.5-3.5	[2]
	TiO <sub>2</sub>		99	123	Au (1.0%), CO (5 atm), 25 °C, 0.8 h	1.9	[3]
	SiO <sub>2</sub>		100(a)		Au (0.16%), H <sub>2</sub> (4 MPa), 140 °C, 3 h	7-9	[7]
	TiO <sub>2</sub>		65	11	Au (1.0%), CO (5 atm), 25 °C, 6 h	n. r.	[5]
	Pristine MWCNTs		94	78	Au (0.3%) NaBH <sub>4</sub> , 90 °C, 4 h	3-10	this work
	TiO <sub>2</sub>		92	15.3	Au (1.0%), HCO <sub>2</sub> NH <sub>4</sub> , 25 °C, 6 h	1.5-3.5	[2]
	TiO <sub>2</sub>		99	99	Au (1.0%), CO (5 atm), 25 °C, 1 h	1.9	[3]
	SiO <sub>2</sub>		100(a)		Au (0.16%), H <sub>2</sub> (4 MPa), 140 °C, 3 h	7-9	[7]
	Pristine MWCNTs		97	81	Au (0.3%) NaBH <sub>4</sub> , 90 °C, 4 h	3-10	this work
	TiO <sub>2</sub>		88	6.9	Au (0.8%), N <sub>2</sub> H <sub>4</sub> , 60 °C, 16 h	n. r.	[1]
	TiO <sub>2</sub>		95	27	Au (1.0%), HCO <sub>2</sub> NH <sub>4</sub> , 25 °C, 3.5 h	1.5-3.5	[2]
	TiO <sub>2</sub>		99	198	Au (1.0%), CO (5 atm), 25 °C, 0.5 h	1.9	[3]

	Fe <sub>3</sub> O <sub>4</sub>		94	188	Au (1.0%), TMDS, 25 °C, 0.5 h	10±3.6	[4]
	SiO <sub>2</sub>		100(a)	-	Au (0.16%), H <sub>2</sub> (4 MPa), 140 °C, 3 h	7-9	[7]
	TiO <sub>2</sub>		90	90	Au (1.0%), CO (5 atm), 25 °C, 1 h	n. r.	[5]
	TiO <sub>2</sub>		93	700	Au (0.1%), NH <sub>3</sub> BH <sub>3</sub> , 25 °C, 1.33 h	n. r.	[6]
	Pristine MWCNTs		98	82	Au (0.3%) NaBH <sub>4</sub> , 90 °C, 4 h	3-10	this work
					No data in bibl.		
	Pristine MWCNTs		95	79	Au (0.3%) NaBH <sub>4</sub> , 90 °C, 4 h	3-10	this work
	TiO <sub>2</sub>		99.0 (a)	-	Au (1.14%), H <sub>2</sub> (10 bar), 100 °C, 1.25 h		[8]
	Fe <sub>2</sub> O <sub>3</sub>		99.4 (a)	-	Au (4.30%), H <sub>2</sub> (10 bar), 100 °C, 1 h		[8]
	TiO <sub>2</sub>		90(b)	9.4	Au (0.8%), N <sub>2</sub> H <sub>4</sub> , 60 °C, 12 h	n. r.	[1]
	TiO <sub>2</sub>		99	28.3	Au (1.0%), CO (5 atm), 25 °C, 3.5 h	1.9	[3]
	TiO <sub>2</sub>		99(a)	82.5	Au (0.2%), H <sub>2</sub> (0.9 MPa), 120 °C, 6 h	n. r.	[9]

	Pristine MWCNTs		61	51	Au (0.3%) NaBH <sub>4</sub> , 25 °C, 4 h	3-10	this work
	TiO <sub>2</sub>		77	45.3	Au (1.0%), HCO <sub>2</sub> NH <sub>4</sub> , 25 °C, 1.7 h	1.5-3.5	[2]
	TiO <sub>2</sub>		98	32.6	Au (1.0%), CO (5 atm), 25 °C, 3 h	1.9	[3]
	Pristine MWCNTs		100	24	Au (0.6%) NaBH <sub>4</sub> , 25 °C, 7 h	3-10	this work
					No data found		

TMDS = tetramethyldisiloxane

n. r. = not reported

(a) conversion values; isolated yields were not reported, thus no TOF values can be calculated

(b) the obtained product is not the expected aminobenzaldehyde, but the product of further condensation of the aldehyde with hydrazine

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