

FUNCTIONALIZED CARBON NANOTUBES AS SUPPORT OF IRIIDIUM-NHC COMPLEXES FOR CATALYSIS APPLICATIONS

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Introduction

Carbon nanotubes (CNT) are defined as graphene sheets rolled up into a cylindrical structure [1]. They have attracted great attention due to their unique properties, such as excellent electrical properties, high stability in most of the reaction media and the possibility to functionalize their (inner and outer) surface with oxygen functional groups. The oxidation of the CNTs can be carried out through multiple oxidative agents (air, plasma, electrochemical methods, redox agents, etc.) [2], but the acid treatments are known to produce large amount of hydroxyl groups in the basal planes and carboxylic acids in the tips, edges and defects of the tubes [3],[4]. There is a huge amount of strategies to functionalize CNTs proposed in the literature, but few of them employ the surface OH-groups mainly via the use of toxic and difficult-handling silane derivatives [5]. There is also a lack of information about covalent bonding of single molecules to the nanotubes using OH-groups, which can be used to covalently attach organometallic complexes acting as catalysts.

N-heterocyclic carbenes (NHC) have recently attracted widespread attention in homogeneous catalysis since they can be used to generate active and stable organometallic complexes [6]. The covalent bonding of the NHC complexes in a solid matrix, i.e. CNTs, developing heterogeneous catalysts, could suppose some advantages, such as an improvement in the catalytic activity, an easily recovery and further cyclability of the catalysts also avoiding leaching processes. Many examples of bonding organometallic complexes using ester or amide bonds with the carboxylic acids of oxidized CNTs have been reported. In addition, the employment of the OH groups is also well known taking advantage of the silane derivatives reactivity. However, there are few cases of organic linkers used to attach the NHC catalysts to the CNTs.

The catalytic hydrogen transfer process is a good strategy for promoting the reduction of C=O and C=N bonds to generate alcohols or amines in mild conditions that avoids the use of hydrogen gas or other dangerous reducing agents [7]. Efficient rhodium and iridium hydrogen transfer catalysts are mainly based on both phosphine and N-donor ligands, although NHC ligands have also been applied to the design of hydrogen transfer catalysts. It has been found that iridium-NHC complexes are more active in the reduction of a wide range of unsaturated compounds than their Rh-NHC analogues for the transfer hydrogenation of unsaturated compounds in 2-propanol/KOH media [8].

In this work, a new way of covalent functionalization of carbon nanotubes is developed, using the surface OH-groups to attach appropriated imidazolium salts by the formation of a labile organic carbonate as intermediate. Thermally

reduced carbon nanotubes at 400 °C in which carboxylic acid groups were removed, were also studied for comparative purposes. In a second step, an iridium NHC complex was immobilized in both supports using [$\{\text{Ir}(\mu\text{-OMe})(\text{cod})\}_2$]. The catalytic activity of the supported catalysts in the reduction of cyclohexanone to cyclohexanol by hydrogen transfer processes was studied over five consecutive cycles, the last one on air atmosphere in order to determine the reusability and stability of the supported catalyst.

Experimental

Materials: Solvents were distilled immediately prior to use from the appropriate drying agents or obtained from a Solvent Purification System (Innovative Technologies). All chemicals, including multiwall carbon nanotubes, were purchased from Aldrich and reagent or HPLC grade was employed in all the experimental work. Raw CVD-grown multiwall carbon nanotubes were oxidized by means of a mixture of sulphuric acid (97%) and nitric acid (60%) in a 3:1 ratio at 80 °C for 20 min, followed by 20 min of ultrasonication. The reaction was quenched with water, and then, the mixture was centrifuged for 30 min at 4700 rpm. The supernatant was discarded, and the remaining solid was washed again with water and centrifuged. The process was repeated until neutral pH to give the parent oxidized carbon nanotubes (CNT). CNT were heated in an electric furnace at 400 °C for 1h, applying a heating ramp of 10 °C min⁻¹ under a nitrogen flow of 100 mL min⁻¹. As result thermally reduced CNT-TR400 were produced. The imidazolium salt [MeImH(CH₂)₃OH]Cl (**1**) [12] and the starting organometallic compound [$\{\text{Ir}(\mu\text{-OMe})(\text{cod})\}_2$] were prepared according to the literature procedures [9].

Functionalization of carbon nanotubes with the imidazolium salt 1: Both type of carbon nanotubes (CNT and CNT-TR400) were functionalized with the imidazolium salt **1** following the same two steps procedure. In a first step, 0.1 g of CNT or CNT-TR400, were dispersed in 20 mL of dichloromethane (DCM). To this dispersion, 15 mmol (3.0225 g) of *p*-nitrophenylchloroformate and 15 mmol (2.1 mL) of triethylamine were added under inert atmosphere. The mixture was cooled to 0 °C with an ice bath and stirred for 24 h, letting the temperature slowly reach room temperature. In a second step, the resulting product was filtered and washed three times with 20 mL of DCM, and was dried for 2 h under vacuum. Then, the resultant solid was dispersed in 15 mL of tetrahydrofuran (THF), to which 70 mg of imidazolium salt **1** was added under inert atmosphere together with a catalytic amount (0.2 mL) of triethylamine. The mixture was refluxed for 24 h. The dispersion was filtered, and the solid was washed with 3x20 mL of THF and 3x20 mL of DCM. The solid was washed with ethanol and dried at 100 °C in a preheated furnace. The samples obtained were labelled CNT-**1** using oxidized carbon nanotubes (CNT) and CNT-TR400-**1** using the thermally reduced nanotubes (CNT-TR400) as respective supports.

Preparation of hybrid catalysts CNT-1-Ir and CNT-TR400-1-Ir: CNT-1 and CNT-TR400-1 were mixed with [$\{\text{Ir}(\mu\text{-OMe})(\text{cod})\}_2$] (0.105 mmol, 69.6 mg) in 10 mL of THF under an argon atmosphere. The mixture was refluxed for 2 days and then immersed into an ultrasonic bath for 30 min. The resultant solid was recovered by centrifugation, washed with THF (5 x 10 mL) and diethyl ether (2 x 5mL) and dried under vacuum to produce CNT-**1-Ir** and CNT-TR400-**1-Ir**.

General procedure for Transfer Hydrogenation Catalysis:

The catalytic transfer hydrogenation reactions were carried out under an argon atmosphere in thick glass reaction tubes fitted with a greaseless high-vacuum stopcock. In a typical experiment, the reactor was charged with a solution of the substrate (5 mmol) in 2-propanol (4.5 mL), internal standard (mesitylene, 70 μ L, 0.5 mmol), base (104 μ L, 0.025 mmol of a KOH solution 0.24 M in 2-propanol) and the catalyst (0.005 mmol, 0.1 mol%). The resulting mixture was stirred at room temperature until complete solution of the catalyst and then placed in a thermostated oil bath at 80 $^{\circ}$ C. Conversions were determined by Gas Chromatography analysis under the following conditions: column temperature 35 $^{\circ}$ C (2 min) to 220 $^{\circ}$ C at 10 $^{\circ}$ C/min at flow rate of 1 mL/min using ultrapure He as carrier gas. The material was recovered by centrifugation and washed with an additional amount of 2-propanol. Several catalytic cycles were repeated with this material without adding any fresh catalyst precursor and at least the last one was performed without inert atmosphere.

Scientific Equipment and Characterization of supports and hybrid catalysts: NMR spectra were recorded on a Bruker Advance 300 or a Bruker Advance 400 spectrometers. ^1H (300.1276 MHz, 400.1625 MHz) and ^{13}C (75.4792 MHz, 100.6127 MHz). The catalytic reactions were analyzed on an Agilent 4890 D system equipped with an HP-INNOWax capillary column (0.4 μm , 25 m x 0.2 mm i.d.) using mesitylene as internal standard. Transmission electron microscopy (TEM) was carried out in a JEOL 2000 EX-II instrument operating at 160 kV; high resolution images of transmission electron microscopy (HRTEM) were obtained in a JEOL-JEM 2100F operating at 200 kV. Elemental analyses were performed on a LECO-CHNS-932 micro-analyser and a LECO-VTF-900 furnace coupled to the micro-analyser. The X-Ray photoemission spectroscopy (XPS) spectra were performed in a SPECS system operating under a pressure of 10^{-7} Pa with a Mg K α X-Ray source. The type of functional groups in the carbon nanotubes was quantified by deconvolution of the C1s XPS peak in Gaussian and Lorentzian functions, assigning 284.4 eV for the graphitic band (Csp 2), 284.8 eV for the defects band (Csp 3), 285.8 eV for the single C-O bond (C-OH), 287.2 eV for the double C-O bond (C=O), 288.5 eV for the carboxylic acids band (COOH) and 289.9 eV for the carbonates band (OCOO) [10]. The amount of iridium present in the samples was determined by means of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in an Agilent 7700x instrument; the samples were digested following the method described by Elgrabi *et. Al* [11].

Results and discussion

Characterization of the parent and functionalized supports

The oxidized carbon nanotubes (CNT) employed in this work have been prepared by an acid treatment of commercial multiwalled nanotubes grown by CVD. For comparative purposes, those nanotubes were also thermally reduced by heating under a nitrogen atmosphere at 400 $^{\circ}$ C for 1 h, which led to the sample CNT-TR400. TEM observations of CNT (Figure 1.a) show nanotubes free of metal catalyst particles and amorphous carbon as a result of the acid treatment. The length of the tubes ranges between 200 and 600 nm, with the diameters varying between 6 and 12 nm (inner and outer diameter respectively). In addition, the tips are opened, which makes the inner cavity accessible.

Interestingly, the thermal treatment does not affect the size and the length of the nanotubes (Figure 1,b). On that way, the thermally reduced sample CNT-TR400 exhibits the same aspect that the oxidized one CNT.

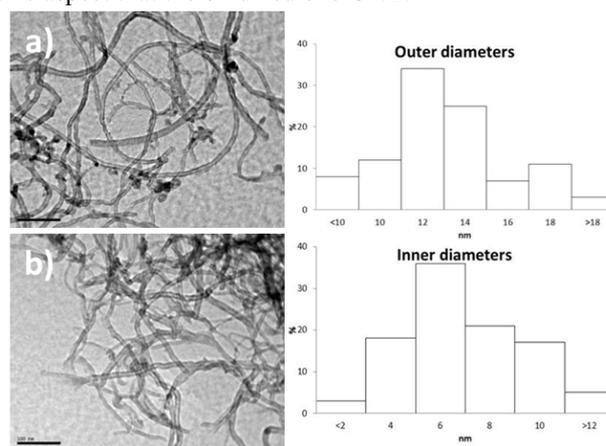
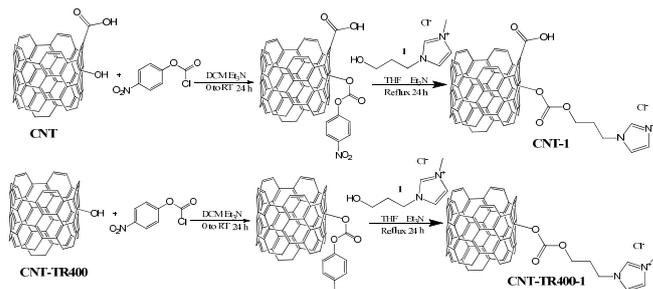


Figure 1. TEM images of: a) parent CNT and b) CNT-TR400, showing the outer and inner diameter distributions for both samples.

The oxygen functional groups introduced during the acid treatment were determined by means of XPS. On one hand, the XPS general spectrum of the CNT reveals a great amount of oxygenated moieties at the external surface of the nanotubes in an atomic ratio C/O of 3 (Table 1), which is considerably reduced during the thermal treatment to produce CNT-TR400. Deconvolution of the high resolution C1s XPS peak indicates that the acid treatment introduced oxygen functional groups are mainly in the form of C-O (10.2 %), which corresponds to hydroxyl groups that are located at the basal planes of the nanotubes. The process also introduce a high amount of carboxylic acids (5.4 %). It is also observed that the thermal treatment eliminates mainly the majority of the carboxylic acids (1.7 %), while other functional groups such as hydroxyl groups, more thermally stable, remain unmodified (10.3 %).

In order to immobilize the organometallic complexes, our strategy consists of the activation of the surface hydroxylic groups with *p*-nitrophenylchloroformate. This strategy proceeds in a first step, via the formation of carbonate. This intermediate can be easily displaced in a second step by a nucleophilic centre (such as the OH-ending of the imidazolium salt (**1**) [12]), as a result of the formation of the leaving group *p*-nitrophenol [13]. The sequence is depicted in Scheme 1. To the best of our knowledge, this strategy has not been employed before with carbonaceous supports.



Scheme 1. Functionalization procedure of the parent CNT with the imidazolium salt **1**.

The successful functionalization with the imidazolium salt **1** was confirmed by $^1\text{H-NMR}$ [14]. The signal corresponding to the imidazolic OH group is not detected in the spectra of **CNT-1** and **CNT-TR400-1**, neither the signals corresponding to the nitrophenol unit. In addition, the signals corresponding to the imidazolium groups are identified. Interestingly, the upfield shifted signals H2 characteristic of imidazolium rings appear at δ 8.65 ppm and for both **CNT-1** and **CNT-TR400-1**. Also, the signal for the aromatic protons of the imidazolium ring are observed at δ 7.40 ppm for both samples **CNT-1** and **CNT-TR400-1**, and with the proper ratio 2:1 comparing with H2. All these data clearly indicate the covalent linkage of the imidazolium to the samples. The amount of the ligand introduced in the samples is determined by elemental analysis. Parent nanotubes **CNT** and **CNT-TR400** have both a nitrogen content of 0.1 %. After functionalization, the amount of nitrogen increases up to 5.6 % for **CNT-1** and 2.5 % for **CNT-TR400-1**, which is consistent with the bonding of the (N-containing) imidazolium ligand. The higher value obtained in the case of **CNT-1** can be attributed to the fact these nanotubes have free carboxylic acids that improve the dispersion capacity of the sample in the polar reaction medium, thus enhancing the conversion degree.

The analysis of the external surface of the functionalized samples by XPS (**Table 1**) reveals the same tendency that was observed for the bulk characterization techniques. An increment in the atomic nitrogen content with respect to the parent **CNT** (from 0.4 % up to 4.7 % in **CNT-1**) and **CNT-TR400** (from 0 % up to 1.7 % in **CNT-TR400-1**) was observed, and it corresponds to the nitrogen in the imidazolium ligand. By comparison with the elemental analysis data previously discussed (which is representative of the total amount of nitrogen present in the sample), the lower nitrogen value might be due to some amount of the imidazolium ligands might be anchored in the inner cavity, inaccessible to the radiation. The deconvolution of the C1s XPS peak of both functionalized samples reveals an increase in the C-O band, located at 285.8 eV, which overlaps the C-N band at 286.0 eV, and in the band positioned at 290.0 eV, attributed to the produced carbonates. Furthermore, the carboxylic band (288.5 eV) remains almost unaltered for both samples **CNT-1** and **CNT-TR400-1**.

These data are indicative of the selectivity of the reaction, since it has only taken place in the hydroxyl functional groups forming the proposed carbonate. Furthermore, the results discard the possible natural esterification between the surface carboxylic acids and the alcohols of the imidazolium salts. In addition, the modification of the wall chemistry due to the thermal reduction does not affect the attachment of the salt.

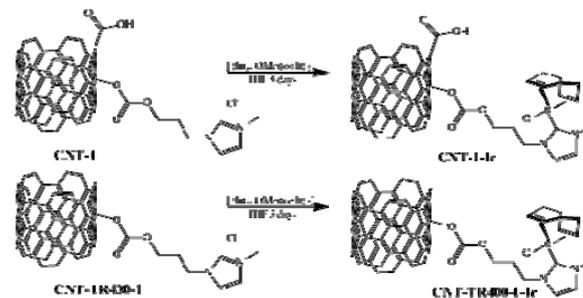
Table 1. XPS data of the parent and functionalized carbon nanotubes.

Sample	CNT	CNT-TR400	CNT-1	CNT-TR400-1
N1s [a]	0.4	0.0	4.7	1.7
%N [b]	0.1	0.1	5.6	2.5
C sp ² [c]	64.4	72.9	48.4	43.9
C sp ³ [c]	17.1	13.8	18.4	27.1
C-O [c]	7.0	7.3	17.2	18.4
C=O [c]	3.2	3.0	3.5	2.9
COOH [c]	5.4	1.6	5.2	1.7
OCOO [c]	2.8	2.6	7.4	7.5

[a] Atomic percentage (%). [b] % determined by elemental analysis. [c] Deconvolution bands of the XPS C1s peak.

Characterization of the iridium hybrid catalysts

The deprotonation of the 2-carbon in the imidazolium heterocycle is a common procedure in the synthesis of NHC carbene complexes [15]. Thus, the imidazolium functionalized nanotubes samples **CNT-1** and **CNT-TR400-1** were reacted with $[\{\text{Ir}(\mu\text{-OMe})(\text{cod})\}_2]$ to produce the hybrid catalyst **CNT-1-Ir** or **CNT-TR400-1-Ir** (**Scheme 2**). For comparative purposes, the reaction of the parent sample **CNT** with $[\{\text{Ir}(\mu\text{-OMe})(\text{cod})\}_2]$ was also studied, which led to the formation of the sample **CNT-Ir**.



Scheme 2. Synthesis of the NHC iridium carbenes supported on the carbon nanotubes.

XPS Ir4f curves corresponding to the hybrid materials are shown in **Figure 2**. The spectra shows two characteristic peaks, the Ir4f7/2 peak centered at 62.4 eV and the Ir4f5/2 centered at 65.6 eV which are typical of Ir (I) compounds. While in the sample which does not contain imidazolium ligand (**CNT-Ir**), the maximum shifts towards higher voltages (63.0 eV for Ir4f7/2), attributed to the presence of some iridium oxide [16] promoted in absence of the imidazolium salt by some oxygen probably present in the CNTs.

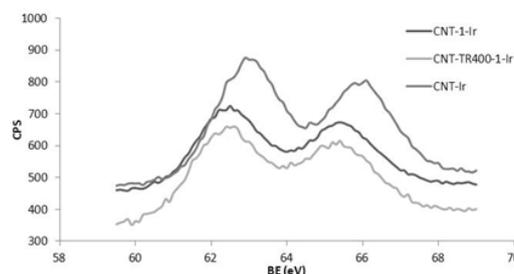


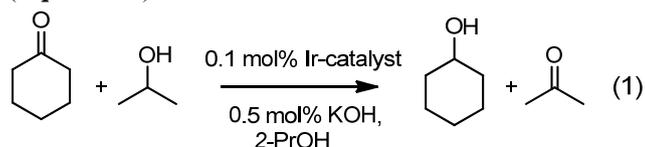
Figure 2. XPS curves of the Ir4f region

The total amount of the iridium in the hybrid nanomaterials was calculated by means of ICP-MS. **CNT-1-Ir** has 10.1 wt.% iridium and **CNT-TR400-1-Ir** has 12.5 wt.% iridium. The sample which has no imidazolium linker, **CNT-Ir**, gives 21 wt.% iridium. Since before treatment with the precursor iridium complex, and the amount of nitrogen in this sample is negligible, the attachment to the nanotube must be different, as discussed above. The maximum amount of iridium that can be loaded in the nanotubes was calculated on the basis of half of the amount of nitrogen introduced in each nanotube using the XPS data in Table 1 (two nitrogens per NHC-carbene ring) and is 19.7 wt.% for **CNT-1-Ir** and 12.9 wt.% for **CNT-TR400-1-Ir**. Comparing both sets of data, it can be concluded that at least one out of two imidazolium rings have reacted with the iridium precursor to give the proposed organometallic complex.

Catalytic activity

The iridium hybrid catalysts, **CNT-1-Ir** and **CNT-TR400-1-Ir**, were tested as catalyst precursors for the reduction of cyclohexanone to cyclohexanol using 2-propanol as hydrogen source (non toxic nature and moderate boiling

point), being at the same time the reaction solvent. Standard catalyst loads of 0.1 mol %, with 0.5 mol % of KOH as co-catalyst and 80 °C of temperature were routinely employed (**Equation 1**).



The reaction times required to reach more than 90% conversion (as determined by GC using mesitylene as internal standard) and the average turnover frequencies (TOF), calculated at the initial time and at 50% conversion, for all the examined catalysts are shown in **Table 2**. Two blank experiments were firstly analysed. As the first blank experiment, the carbon material **CNT-1**, i.e. CNT functionalized with the imidazolium salt 1 but without iridium was used. The reaction under these conditions logically led to 0 % conversion after 3 hours (**Table 2**). The second blank experiment was performed using **CNT-Ir** as catalyst, which contains no NHC-carbene-linker between the carbon material and iridium. As can be observed in **Table 2** only 10 % conversion was achieved after 3 hours of reaction. It was therefore confirmed that the presence of the carbene is necessary to obtain an efficient catalyst.

Table 2. Catalytic Hydrogen Transfer from 2-Propanol to Cyclohexanone with Iridium Hybrid Catalysts

Catalyst	Time [min]	Conversion [%]	TOF ₀ [h ⁻¹][a]	TOF ₅₀ [h ⁻¹][b]
CNT-1-Ir	210	93	4730	1220
CNT-TR400-1-Ir	130	94	5400	3000
CNT-Ir	180	10	30	-
CNT-1	180	0	-	-

Turnover frequencies calculated at [a] the initial time and [b] at 50% of conversion

As can be seen in **Table 2**, both hybrid catalysts were found to be active in the transfer hydrogenation of cyclohexanone to cyclohexanol. This fact proofs that the new functionalization method described in this work could generate active hybrid catalysts. The catalytic performance is similar to homogeneous and heterogeneous systems developed in our group.[12], [18] It is interesting to mention however, that the thermally reduced material is more active than the corresponding oxidized support, achieving > 93% of conversion in 130 min *versus* 210 min that needs **CNT-1-Ir**. The initial TOFs was 4730 h⁻¹ for **CNT-1-Ir** and 5400 h⁻¹ for **CNT-TR400-1-Ir**.

The transfer hydrogenation of cyclohexanone was monitored at different time intervals. As can be observed in **Figure 3**, no induction period was detected, as the reduction of cyclohexanone was observed immediately after thermal equilibration of the reactant mixture. In general, the kinetic profiles are very similar. The thermally reduced catalyst **CNT-TR400-1-Ir** is the most active specie at any time. These data totally agree with the reactions times and calculated TOFs show in **Table 2**. The presence of free carboxylic acids seems therefore to difficult the kinetics of the catalytic process.

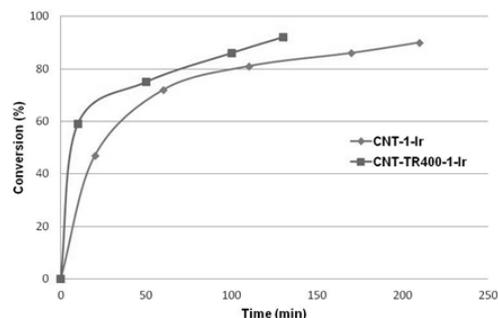


Figure 3. Reaction profiles for transfer hydrogenations of cyclohexanone by the hybrid catalysts.

Recycling studies were carried out with both nanotube-supported iridium-NHC catalysts. The black solids obtained after the catalysis were filtered and washed with fresh 2-propanol (4 x 5 mL), and then subjected to another catalytic cycle by addition of further cyclohexanone. The sample **CNT-Ir** was inactive when it was submitted to the second catalytic cycle. However, both NHC-supported catalysts **CNT-1-Ir** and **CNT-TR400-1-Ir** exhibited the same catalytic activity than the fresh catalysts after 4 consecutive cycles under an argon atmosphere (**Figure 4**), with comparable conversions after the same time (210 minutes for **CNT-1-Ir** and 130 minutes for **CNT-TR400-1-Ir** in the five cycles performed), with identical reaction profiles. Furthermore, in sharp contrast with the air-sensitivity of the homogeneous iridium-NHC based catalysts, these CNT-supported catalysts were stable in air, obtaining quantitative conversion of cyclohexanone when the catalytic reactions were conducted under an air atmosphere in an additional final fifth cycle.

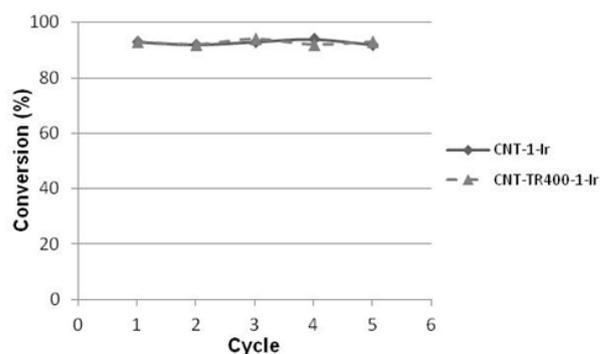


Figure 4. Catalysts recyclability and stability studies. Note: the fifth cycle is performed in air.

Conclusions

We have demonstrated that the surface hydroxylic groups generated by an acid oxidation of multiwall carbon nanotubes can be used to covalently bond iridium NHC organometallic complexes by a two-step procedure via the use of *p*-nitrophenylchloroformate. Thermally reduced CNTs at 400 °C, in which the carboxylic acids were eliminated, exhibit a similar functionalization extent which confirms the selectivity of the procedure. Moderate to good conversions were obtained in the introduction of the imidazolium salts and in the anchoring of the final iridium NHC complex.

The new hybrid materials were active as catalysts in the transfer hydrogenation of cyclohexanone, reaching complete conversion and similar catalytic performance than homogeneous and heterogeneous systems developed before.

Thermally reduced materials were found to be the most active support which indicates the negative effect of carboxylic acids in the catalytic process. Finally, all the samples studied were stable through successive catalytic cycles, which confirm that the catalyst can be reused in consecutive runs without any loss of activity, even under an air atmosphere.

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