

# Catalytic activity of iridium NHC complexes covalently bonded to carbon nanotubes and graphene oxide

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## INTRODUCTION

Carbon nanotubes and graphene have been extensively applied as proactive supports to generate heterogeneous catalysts. Both exhibit a carbon structure composed by carbon atoms with sp<sup>2</sup> hybridization and both are used in similar applications, as in catalysis. However, the role of each particular substrate, determined by its structural peculiarities, can be different and should be studied for each particular catalytic reaction and in their structure. The aim of this work is to study the differences between oxidized carbon nanotubes (CNT) and graphene oxides (GO) as proactive supports of iridium N-heterocyclic carbene (NHC) catalyst. The effect of their inherent structure in the catalytic activity in hydrogen transfer reactions was studied in detail.

## MATERIALS AND METHODS

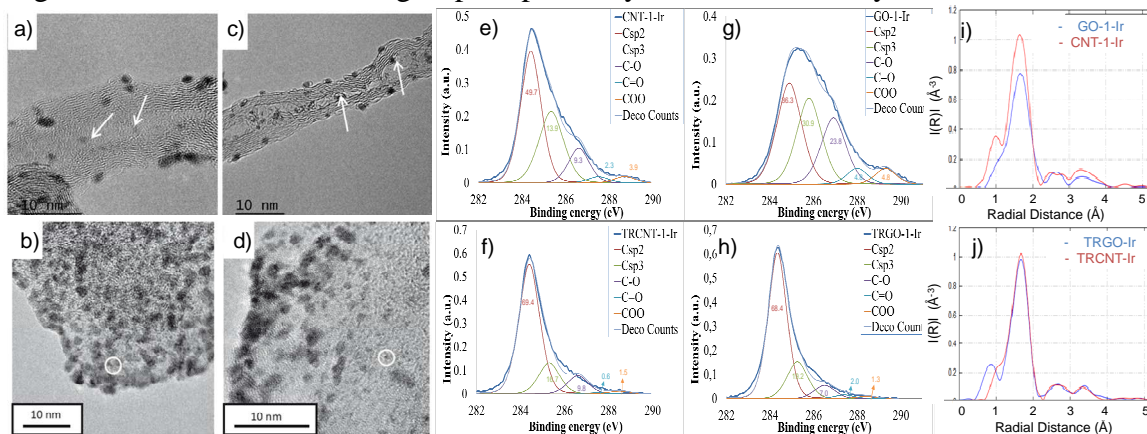
GO was obtained by a modified Hummers method [1] and CNT was prepared by acid treatment of commercial carbon nanotubes [2]. The thermal treatment at 400°C of GO and CNT led to the partially reduced samples TRGO and TRCNT, respectively. [MeImH(CH<sub>2</sub>)<sub>3</sub>OH]Cl (**1**) and [Ir(μ-OMe)(cod)]<sub>2</sub> were prepared according to the literature [3]. Initially, the four materials were covalently functionalized in a three-step procedure. 0.1 g dichloromethane (DCM) suspensions were mixed with 15 mmol of *p*-nitrophenylchloroformate and 15 mmol of triethylamine was added and stirred for 24 h. The filtered product was dried under vacuum. In a second step, the solid was dispersed in 15 mL of tetrahydrofuran (THF), to which 70 mg of imidazolium salt **1** was added together with a catalytic amount (0.2 mL) of triethylamine, and refluxed for 24 h. The filtered solid was washed and dried at 100 °C. The product dispersed in 10 mL of THF, was mixed with [Ir(μ-OMe)(cod)]<sub>2</sub> (0.15 mmol, 100 mg) and refluxed for 2 days. The resultant solid was recovered by centrifugation, washed with THF and ether and dried under vacuum. Samples **CNT-1-Ir**, **TRCNT-1-Ir**, **GO-1-Ir** and **TRGO-1-Ir** were generated. The samples were characterized by TGA, elemental analysis, HRTEM, EXAFS and XPS.

The supported Ir complexes were studied in the catalytical reduction of cyclohexanone to cyclohexanol. In a typical experiment, the reactor was charged with cyclohexanone (0.52 mL, 5.0 mmol), solvent (2-propanol, 4.5 mL), internal standard (mesitylene, 70 μL, 0.5 mmol), base (0.1 mL, 0.025 mmol of a KOH solution 0.24 M in 2-propanol) and the catalyst (0.005 mmol, 0.1 mol%). Conversions were determined by gas chromatography analysis.

## RESULTS AND DISCUSSION

The functionalization of carbon nanomaterials led to the formation of the iridium NHC complexes covalently attached to the OH groups present in the surface, confirmed by the presence of two maxima in the XPS Ir4f spectra, at 62.5 and 65.6 eV, which correspond to Ir(I) species. This is consistent with the HRTEM analysis (Fig. 1a-d). The

fitting of the XPS C1s spectra (Fig. 1e-h) confirms the reduction in the oxygen functional groups of the TRGO and TRCNT species. Additionally, the larger amount of  $Csp^2$  bonds in nanotubes than in graphenes is also evidenced. EXAFS curves of the Ir complexes (Fig. 1i,j) show the formation of the same first coordination sphere on the Ir complex in all cases. However, differences in the long range interactions are observed, possibly related to the influence of the support. In general, high degree of disordered is obtained when oxidized supports are used, and particularly in GO, which is in agreement with the chemical groups depicted by the XPS C1s analysis.



**Fig.1** Characterization of NHC-functionalized supports.

All catalysts were active in the reduction of cyclohexanone to cyclohexanol by a hydrogen transfer process (Table 1), being also stable under air and recyclable after 5 consecutive cycles. The use of reduced supports gave rise to a better catalytic performance (conversions of 95% in shorter time than oxidized species, 120-150 min). This better performance could be due to their more reconstructed  $csp^2$  structure and their fewer amount of structural defects and oxygen functional groups, giving rise to an Ir catalyst with more order in its local environment.

**Table 1.** Catalytic performance of GOs and CNTs with recycling studies.

Sample	Time (min)	4 cycles Conv.	Air Conv.	TON	TOF <sub>0</sub> (h <sup>-1</sup> )	TOF <sub>50</sub> (h <sup>-1</sup> )	TOF <sub>90</sub> (h <sup>-1</sup> )
<i>CNT-1-Ir</i>	210	92	92	934	11214	1220	267
<i>GO-1-Ir</i>	760	92	94	947	11364	758	75
<i>TRCNT-1-Ir</i>	120	91	93	942	11336	3000	471
<i>TRGO-1-Ir</i>	150	93	92	964	11568	1607	385

## CONCLUSIONS

Iridium NHC complexes were supported onto CNTs and GOs by covalent attachment to their OH groups. All supported complexes were active in the catalytic transformation of cyclohexanone to cyclohexanol, stable under air and recyclable after 5 cycles. The catalytic activity of catalysts supported on CNTs is higher, and it is enhanced when reduced supports are used. A more reconstructed aromatic structure of the support and fewer oxygen groups seem to positively affect the catalytic reaction.

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