

# Thesis Review. Covalent functionalization of carbon nanotubes and graphene for catalysis applications

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## OBJECTIVES AND NOVELTY

Carbon nanotubes (CNT) and graphene are recently discovered carbon nanomaterials which find application in a great number of fields. Their excellent mechanical, electrical, thermal and chemical properties make them useful for a wide range of new developments which move from electronic devices to drug-delivery systems. In addition, catalytic systems usually employ carbon nanotubes and graphene in any of the stages of the catalytic process.

In this work, the integration of carbon nanotubes and graphenic materials in well-known homogeneous catalytic systems, *i.e.* unsaturated-substrates reduction reactions by means of hydrogen transfer processes catalyzed with iridium N-heterocyclic carbene complexes is studied. The employment of different strategies for the preparation of the supports, the design of the nanostructure functionalization routes with the metallic complexes and the study of the catalytic activity of the final hybrid materials are described. Both types of materials were oxidized with the aim of developing oxygen functional groups which allow nanomaterial functionalization methods to be applied with the organometallic compounds. A special effort was made to accomplish a complete and exhaustive characterization of the involved samples by typical solid characterization techniques.

## RESULTS

The treatment of carbon nanotubes using reagents with increased oxidation degree led to a proportional increment in the oxygen functional groups at the surface and at the tips of the nanotubes. Only the strongest oxidizing agent introduced more oxygen functional groups in the CNT. These facts modified the capacity of forming stable suspensions in water and they also modify the adsorption behavior. Thus, in the comparative study of benzene adsorption, employed as an additional characterization technique, the most oxidized CNT exhibited faster kinetics and higher adsorption capacity.

The great amount of oxygen moieties introduced in the most oxidized carbon nanotubes allows the functionalization through their carboxylic groups in order to generate new hybrid materials with supported molecular catalysts. They presented enhanced catalytic activity in the reduction reaction of cyclohexanone to cyclohexanol compared to their corresponding homogeneous systems. Figure 1 shows the possible structure of one of the hybrid systems and the comparison in the catalytic activity of the heterogeneous and homogeneous samples. Moreover, they also present excellent cyclability and air stability, in sharp contrast with their analogous non-supported catalysts.

The synthesis of hybrid catalysts supported on graphene oxide was based in a new functionalization

strategy, which consists in the modification of the surface hydroxyl groups employing organic-based connectors. The selectivity of the reaction was checked by the functionalization of the corresponding thermally reduced materials which do not possess carboxylic acids. The later were those which presented the best catalytic activity, superior to the homogeneous systems too. In addition, both hybrid catalysts also presented cyclability and air stability. This new functionalization procedure was also confirmed by obtaining analogous supported iridium catalysts on oxidized and thermally reduced carbon nanotubes, which were more active on the same catalytic process. On Figure 2 is schemed the comparison of both types of carbon nanostructures functionalized under the same strategy.

The study of the local environment of the iridium organometallic complexes anchored on the carbonaceous support revealed a direct bond between the metal and the supports, which affects the catalytic activity of the system (Figure 3). The presence of structural defects in the aromatic lattice was demonstrated to generate catalysts with poor activities. Partially reduced materials based catalysts achieved the best performances. Moreover, the correct type and amount of oxygen functional groups are necessary to obtain a good behavior in order to establish stabilizing bonds between those groups and the metallic center.

## CONCLUSIONS

Different iridium NHC organometallic complexes can be introduced in the surface oxygen functional groups of carbon nanomaterials, such as oxidized carbon nanotubes and graphene oxide. An adequate oxygen-surface chemistry development is necessary to obtain a good metallic load on the surface of the support. The supported organometallic complexes are stable and active catalysts in the reduction processes by means of hydrogen transfer.

The catalytic activity of those complexes bonded to the material, through the carboxylic and hydroxilic moieties, is similar or better than the corresponding homogeneous systems. In addition, the catalysts become stable in non-protected atmospheres, and the heterogenization allows the reuse of the catalysts due to the obtaining of the same times after the successive-cycles performance.

The local environment of the metal and the surface chemistry of the material determine the catalytic activity. Although all the NHC complexes-containing samples obtained complete conversions, only the faster catalysts were those which presented an adequate distribution of oxygen groups and structural defects. An excessive oxidation which generates free carboxylic acids, or ineffective which does not provide the required surface oxygen or defects on the material, leads to less efficient catalysts.

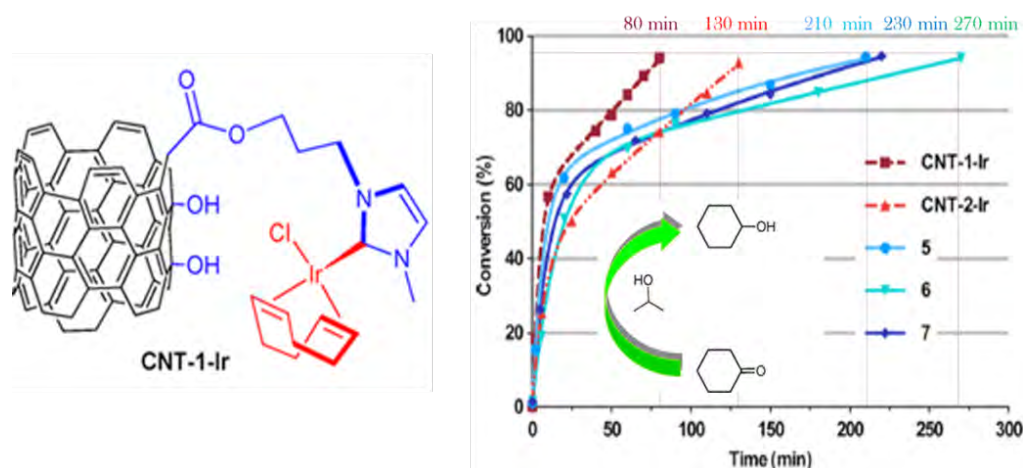


Figure 1. Structure of CNT-1-Ir sample and the catalytic activity in the reaction studied.

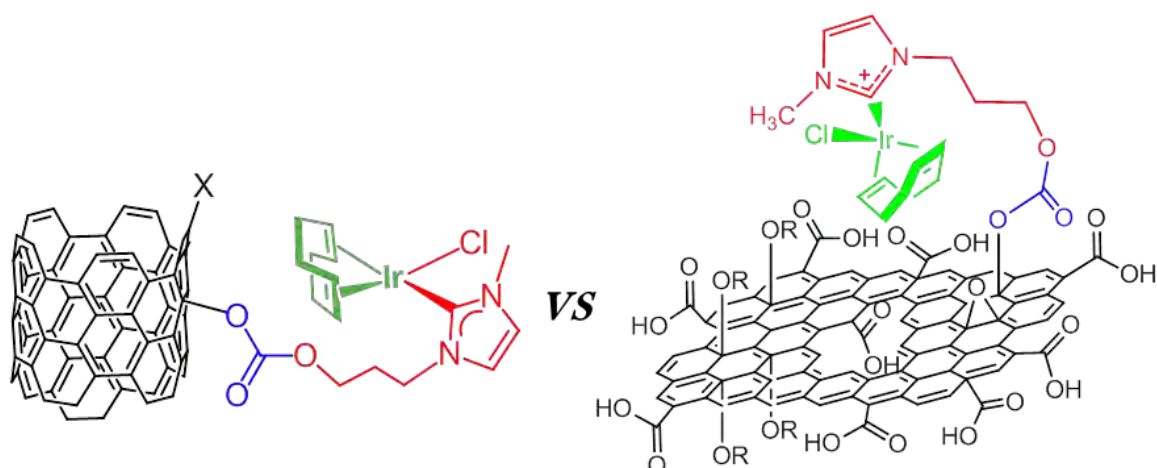


Figure 2. Structure of carbon hybrid materials functionalized in their OH groups

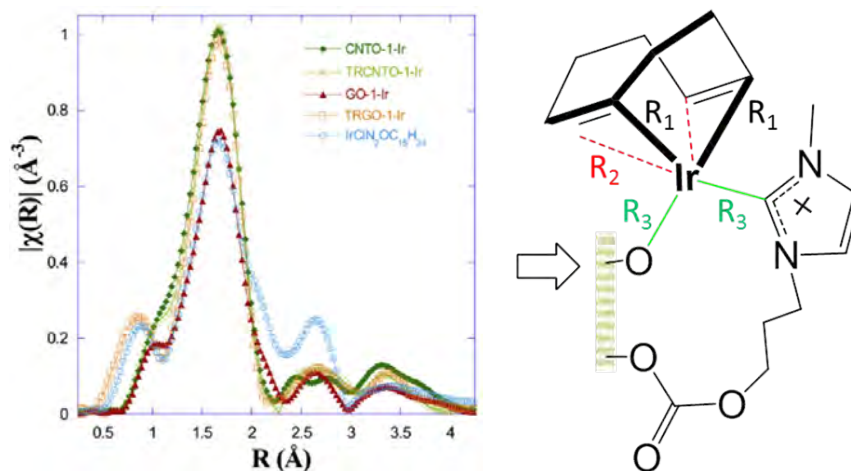


Figure 3. EXAFS data that allow revealing the actual structure of the hybrid systems covalently bonded to the carbon nanomaterials

## RELATED PUBLICATIONS

<sup>1</sup> M. Blanco, P. Álvarez, C. Blanco, M.V. Jiménez, J. Fernández-Tornos, J.J. Pérez-Torrente, L.A. Oro, R. Menéndez. Enhanced Hydrogen-Transfer Catalytic Activity of Iridium N-Heterocyclic Carbenes by Covalent Attachment on Carbon Nanotubes. *ACS Catal.* **2013**, 3, 1307-1317.

<sup>2</sup> M. Blanco, P. Álvarez, C. Blanco, N. Campos, D. Gómez, R. Menéndez. Influence of the alignment degree of CVD-grown carbon nanotubes on their functionalization and adsorption capacity. *Diamond and Related Materials*, **2013**, 37, 1-7.

<sup>3</sup> M. Blanco, P. Álvarez, C. Blanco, M.V. Jiménez, J. Fernández-Tornos, J.J. Pérez-Torrente, L.A. Oro, R. Menéndez, Graphene-NHC-iridium hybrid catalysts built through -OH covalent linkage, *Carbon*, **2015**, 83, 21-31.

<sup>4</sup> M. Blanco, P. Álvarez, C. Blanco, M.V. Jiménez, J. Fernández-Tornos, J.J. Pérez-Torrente, L.A. Oro, J.

Blasco, G. Subías, V. Cuartero, R. Menéndez. "Effect of structural differences of carbon nanotubes and graphene based iridium-NHC materials on the hydrogen transfer catalytic activity" *Carbon*, **2016**, 96, 66-74.

<sup>5</sup> J. Blasco, V. Cuartero, G. Subías, M. V. Jiménez, J. J. Pérez-Torrente, L. A. Oro, M. Blanco, P. Álvarez, C. Blanco, R. Menéndez. "Local structure of Iridium organometallic catalysts covalently bonded to carbon nanotubes" *Journal of Physics, Conference series*. **2015**, Submitted.

<sup>6</sup> M. Blanco, P. Álvarez, C. Blanco, M.V. Jiménez, J. Fernández-Tornos, J.J. Pérez-Torrente, L.A. Oro, R. Menéndez. "Enhancing the hydrogen transfer catalytic activity of hybrid carbon nanotube-based NHC-iridium catalysts by increasing the oxidation degree of the nanosupport". *RSC Catalysis, Science and Technology*, **2015**, Submitted.

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