

The effect of the support in the catalytic activity of iridium NHC complexes covalently bonded to carbon nanotubes and graphene oxide

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Abstract

Carbon nanomaterials, highlighting carbon nanotubes (CNT) and graphene oxide (GO), have been recently applied as supports to generate proactive heterogeneous catalysts [1],[2]. However, the aromatic degree of the support structure and the amount of oxygen functional groups could play an important role in the catalytic performance. In this work, both carbon nanomaterials are covalently modified through their surface OH groups to develop active catalysts based on supported iridium N-heterocyclic carbene (NHC) complexes. The effect of the inherent structure of the support will be studied.

GO [2] obtained by a modified Hummers method, acid-oxidized CNT [1] and their corresponding 400 °C thermally reduced materials were covalently functionalized with an appropriate hydroxyl-ending imidazolium salt through their OH functional groups. Characterization of the imidazolium-modified samples using typical solid characterization techniques, such as TGA, elemental analysis or XPS, enables the amount of the imidazolium compounds in the nanomaterials to be determined with moderate to good conversions. In both cases, nanotubes exhibit a better aromatic structure presenting also fewer amounts of oxygen functionalities.

Both samples were used to generate in situ iridium NHC complex derived from the later imidazolium salt. XPS and HRTEM analysis confirm the presence of the iridium NHC complexes bonded to the samples. The supported complexes were tested in the reduction of cyclohexanone to cyclohexanol by means of hydrogen transfer processes with 2-propanol/KOH as heterogeneous catalysts. The samples were found to be active in the reaction conditions, giving conversions over 90 % in the times depicted in table 1. However, CNT catalysts exhibit a better performance than their corresponding GO. The better sp² structure of the tubes, combined with their fewer amount of structural defects and oxygen functional groups could be the responsible. Finally, good cyclability of the catalysts without any loss of activity and a good stability in air were observed, in sharp contrast with the poor air stability of the related homogeneous system developed before.

References

- [1] M. Blanco, P. Álvarez, C. Blanco, M. V. Jiménez, J. Fernández-Tornos, J. J. Pérez-Torrente, L. A. Oro, Rosa Menéndez ACS Catal. **3** (2013), 1307.
[2] M. Blanco, P. Álvarez, C. Blanco, M. V. Jiménez, J. Fernández-Tornos, J. J. Pérez-Torrente, L. A. Oro, Rosa Menéndez. Carbon **83** (2015), 21.

Figures

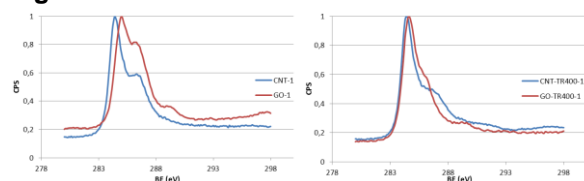


Figure 1. XPS C1s of functionalized oxidized and reduced supports

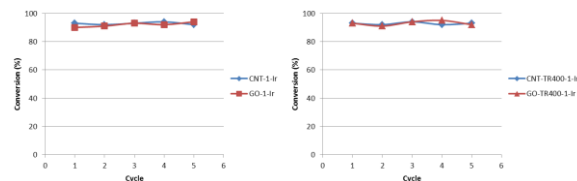


Figure 2. Recycling studies of the catalysts.

Table 1. Catalytic performance

Sample	Time for 90% (min)	TON	TOF ₀ (h ⁻¹)	TOF ₅₀ (h ⁻¹)	TOF ₉₀ (h ⁻¹)
CNT-1-Ir	210	934	11214	1220	267
GO-1-Ir	760	947	11364	758	75
CNT-TR400-1-Ir	120	942	11336	3000	471
TRGO-1-Ir	150	964	11568	1607	385
CNT-Ir	-	101	30	-	-
CNT-TR400-Ir	-	70	21	-	-
GO-Ir	-	147	441	-	-
GO-TR400-Ir	-	203	609	-	-

Acknowledgments

The authors thank MICINN (Projects CONSOLIDER INGENIO 2010 CSD2009-00050, MAT2010-16194 and CTQ 2010-15221), and the Diputación General de Aragón (E07) for their financial support. Dr. Patricia Álvarez thanks MICINN for her Ramón y Cajal contract. Matias Blanco acknowledges his fellowship from and MECD (AP2010-0025).