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Graphene Oxide as promoter for chemical reactions monitored by X-Ray Photoelectron spectroscopy

Alessandro Kovtun[1], Lorenzo Lombardi[2], Laura Favaretto[1], Cristian Bettini[1], Manuela Melucci[1], Vincenzo Palermo[1],Marco Bandini[2],
Organization, Address, City, Country (Calibri 12)
Istituto per la Sintesi Organica e Fotoreattività (ISOF) - CNR, via Gobetti 101, 40129 Bologna, Italy
Dipartimento di Chimica "G. Ciamician"- Università di Bologna, via Selmi 2, 40126 Bologna, Italy
alessandro.kovtun@isof.cnr.it

Graphene Oxide (GO) presents an extremely rich and complex chemical structure, this one-atom thick material is composed by large sp^2 aromatic region (few nm) surrounded by a plethora of defective Carbon atoms arranged in different chemical moieties: C-C sp^3 defects, hydroxyl, epoxy, carbonyl and carboxyl groups[1]. Such chemical variety offers a unique opportunity for chemical functionalization and carbocatalysis, but the mechanisms behind this phenomena are non-trivial issues. The ability to quantify the different chemical groups is the key for a complete understanding of reaction path and mechanisms. Unfortunately, only few spectroscopic techniques allow a quantitative study of GO structure: Solid State Nuclear Magnetic Resonance Spectroscopy and X-Ray[1] Photoelectron Spectroscopy[2] (XPS).
In this framework we present two distinct case studies reactions that involve the role of GO: i) the allylic alkylation of thiophenes with alcohols by using Friedel–Crafts-type protocol[3] and ii) the site-selective allylative and allenylative dearomatization of indoles with alcohols under carbocatalytic regime[4,5]. In both cases, by using XPS data, we found that the covalent activation was the main reaction mechanism, moreover, the mechanistic view was further supported by using density functional theory calculations based on XPS data.

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Figures

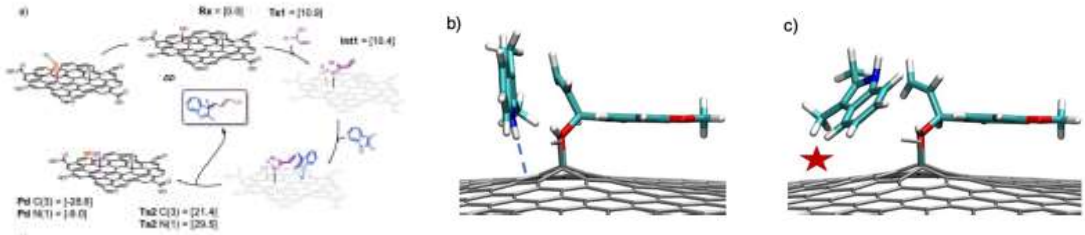

Figure 1: (a) Schematic representation of the reaction mechanism. The energies of the identified critical points in square bracket (kcalmol@1); 3D representation of the identified transition states for the C(3) (b) and (N1) (c) attack of the indoles. Figure adapted from reference[4].