



Nickel nanoparticles supported on graphene as catalysts for aldehyde hydrosilylation



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ABSTRACT

Nickel nanoparticles (NPs) supported on different undoped or doped with N or B graphenes (Gs) have been tested as catalyst for the hydrosilylation of aldehydes to obtain the corresponding siloxanes with high conversion and good selectivity in short reaction time. The different Gs employed were obtained by pyrolysis under inert atmosphere of alginate or chitosan, modified or not with boric acid. Then the metal NPs obtained by polyol reduction method using ethylene glycol were adsorbed on Gs. The Ni-containing G catalysts were characterized by electron microscopy, XPS and Raman spectroscopy. The scope of the Ni/G catalyst includes aliphatic and aromatic aldehydes as well as a variety of hydrosilanes.

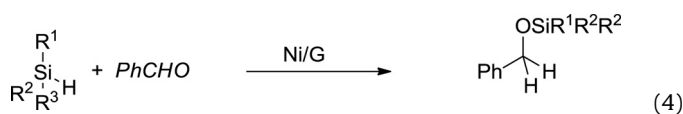
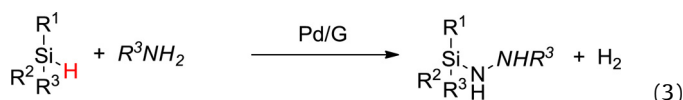
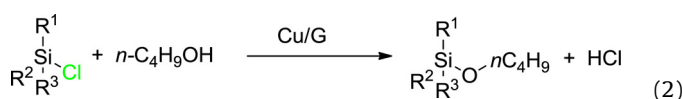
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1. Introduction

Due to its large surface area, extended π orbitals, 2D morphology and high dispersability, graphene (G) and related materials are suitable supports of metal nanoparticles (MNPs) exhibiting high catalytic activity [1–7]. In some cases, it has been found that the activity of MNPs supported on G is better than the activity of these MNPs on other supports including different types of carbon nanoforms and metal oxides [3,4,7,8]. On one hand, overlap between the p and d orbitals of transition metal with π orbitals of G can modulate the electronic density on the MNPs and also may result in a strong metal–support interaction necessary to avoid leaching and minimize MNP size growth. On the other hand, the adsorption capacity of G bringing substrates and reagents near the active MNP can contribute to increase the reaction rates.

Recently, we have reported that Cu NPs supported on G is a highly efficient catalyst to promote the dehydrogenative coupling of alcohol with hydrosilanes (Eq. (1)) [9]. This reaction has the advantage over the conventional silylation (Eq. (2)) of overcoming the use of halosilanes and minimizing the production of corrosive

byproducts (HX), increasing atom efficiency. Although Pd exhibits higher activity than Cu for the oxidative coupling of silanes and alcohols, Cu as catalyst has advantages in terms of affordability and sustainability. Similarly, the dehydrogenative coupling of hydrosilanes and amines (Eq. (3)) has also been recently reported using Pd supported on G as catalyst [10]. For both processes, it was found that G as support leads to a more efficient catalyst than when the MNPs are deposited on other materials.



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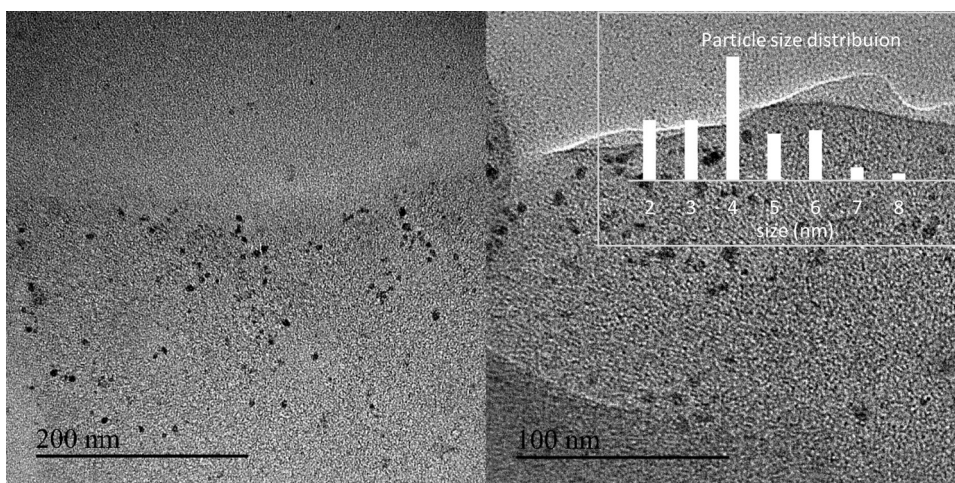


Fig. 1. Two TEM images at different magnification taken for Ni/G. The inset shows the size distribution of Ni NPs.

Continuing with this line of research aimed at exploiting the potential of Gs as support of MNPs, in the present manuscript we describe that Ni NPs supported on G is a convenient catalyst for the addition of silanes to aromatic aldehydes. This reaction (Eq. (4)) is similar to the Strecker addition of halosilanes to aldehydes catalyzed by diluted acids. Also in this case, the hydrosilylation has the advantage of avoiding halosilanes as reagents.

2. Experimental

2.1. Catalysts synthesis and characterization

As supports of MNPs and based on related precedents for the dehydrogenative coupling of hydrosilanes and alcohols or amines [9,10], a G obtained by exfoliation of turbostratic graphitic carbon obtained by pyrolysis of alginate was used. In addition, B- and N-doped Gs [(B)G and (N)G, respectively] were obtained pyrolysing the borate ester of alginate [(B)G] or chitosan [(N)G] at 1000 °C under inert atmosphere, followed by exfoliation of the graphitic carbon residues by sonication [11–13]. For the sake of comparison graphene oxide (GO) prepared from graphite by Hummers oxidation and exfoliation was also included as support in the study [14].

All these Gs are well documented in the literature and had been previously used as metal-free catalysts or as support of MNPs [9,10,15–17]. The G samples employed in the present study were characterized by TEM, AFM, Raman and XPS and their properties coincide with those reported in the literature for these G samples [10,18–21].

MNPs were obtained by the polyol method consisting in the reduction of salts of the corresponding metals in hot ethylene glycol [22]. Deposition was performed simultaneously to the formation of the MNPs by suspending the corresponding G in ethylene glycol at the same time that the reduction of the metal ions is taking place [22]. In the present study, MNPs of Cu, Ni and Pd supported on various Gs were prepared. The Cu/G and Pd/G catalysts correspond to those samples previously reported in the literature [9,10]. G-supported catalysts were analyzed to determine the metal content that was 5 wt% in all cases. TEM allowed determining the morphology and average MNP size and XPS was used to establish the oxidation state of Ni. The single layer morphology of Ni/G was established by AFM.

The Ni NPs employed as catalysts for the addition reaction between the aldehyde and the hydrosilane were supported on the G samples following the synthesis described in the literature [10].

Accordingly, a suspension in ethylene glycol of graphene and the metal precursor, NiCl₂, was sonicated for 1 h. After sonication the mixture was heated at 120 °C for 24 h at reflux temperature. Ni NPs are formed by reduction of ethylene glycol and becoming spontaneously deposited on G in the same step.

2.2. Catalytic tests

The corresponding catalyst (0.06 mmol% of metal respect to substrate) was introduced in an ampoule equipped with a magnetic bar. The aldehyde (10 mmol) was added under argon atmosphere and the ampoule was sonicated for 30 min. Then, hydrosilane (5 mmol) and dodecane as internal standard were added to the ampoule and the reactor sealed. The reaction mixture was magnetically stirred at 120 °C in an oil bath preheated at the reaction temperature. At the end of the reaction, the reaction mixture was cooled to room temperature and an aliquot of 0.1 mL was diluted with anhydrous toluene (0.5 mL), filtered, and injected into GC, determining the conversion and product yields based on the internal standard. The rest of the reaction mixture was filtered and the liquid phase diluted in deuterated chloroform and analysed by ¹H NMR spectroscopy (Varian Gemini 300 MHz) to determine product selectivity. Supporting information contains spectroscopic data of the hydrosilylation products **3a–h**.

3. Results and discussion

As support of MNPs and based on related precedents for the dehydrogenative coupling of hydrosilanes and alcohols or amines [9,10], a G obtained by exfoliation of turbostratic graphitic carbon resulting from pyrolysis of alginate was initially used. Two additional doped Gs, (B)G and (N)G, were obtained pyrolysing at 1000 °C under inert atmosphere the borate ester of alginate [(B)G] and chitosan [(N)G], followed by exfoliation of the graphitic carbon residues by sonication [11,13]. For the sake of comparison GO prepared from graphite by Hummers oxidation and exfoliation was also included as support in the study [14].

All these Gs are well documented in the literature and had been previously used either as metal-free catalysts or as support of MNPs [9,10,15–17]. The G samples employed in the present study were characterized by chemical analysis, TEM, AFM, Raman and XPS and their properties coincide with those reported in the literature for these G sample [10,18–21].

MNPs were obtained by the polyol method consisting in the reduction of the salts of the corresponding metals in hot ethylene

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