



Review

Metal nanoparticles supported on two-dimensional graphenes as heterogeneous catalysts



Sergio Navalon^a, Amarajothi Dhakshinamoorthy^{b,1}, Mercedes Alvaro^a,
Hermenegildo Garcia^{a,*}

^a Instituto Universitario de Tecnología Química CSIC-UPV and Departamento de Química, Universidad Politécnica de Valencia, Av. De los Naranjos s/n, Valencia 46022, Spain

^b School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India

Contents

1. Introduction and scope of the review	100
2. Uniqueness of Gs as supports for MNPs	101
3. Interaction of MNPs with Gs	102
4. Preparation of supported MNPs on Gs	104
4.1. Preparation of GO and Gs	104
4.2. Deposition of MNPs on Gs	104
5. Influence of particle size and morphology of G-supported MNPs on catalysis	105
6. Best practices in the use of MNPs supported on Gs as catalysts	106
7. General overview of G-supported MNPs as catalysts	107
8. G-supported MNPs as catalysts	107
8.1. Oxidation reactions	107
8.1.1. Aerobic oxidation	107
8.1.2. CO oxidation	117
8.1.3. Oxidation reactions promoted by oxidants other than oxygen	118
8.1.4. MNPs supported on Gs as catalysts for H ₂ O ₂ activation	119
8.1.5. MNPs on Gs as catalysts for PMS decomposition	120
8.2. Reduction reactions	121
8.2.1. Hydrogenation reactions	121
8.2.2. Reduction reactions	125
8.2.3. Catalytic reduction of 4-nitrophenol	126
8.2.4. Catalytic reduction of 2-nitroaniline	129
8.2.5. Catalytic reduction of various nitroarenes	129
8.3. Coupling reactions	130
8.3.1. Suzuki–Miyaura cross-coupling	130
8.3.2. Heck and/or Suzuki–Miyaura cross-coupling	131
8.3.3. Sonogashira, Heck, and/or Suzuki–Miyaura cross-coupling	133
8.3.4. Miscellaneous couplings	133
8.4. Hydrogen release/storage reactions	135
8.4.1. H ₂ production from AB and derivatives	137
8.4.2. H ₂ production from miscellaneous sources	138
8.5. Tandem reactions promoted by Gs	140
8.6. Asymmetric catalysis by G-related materials	142
8.7. Miscellaneous reactions	143
9. Conclusions and future prospects	143
Acknowledgements	144
References	144

* Corresponding author. Tel.: +34 620952690.

E-mail address: hgarci@qim.upv.es (H. Garcia).

¹ Joint first author.

ARTICLE INFO

Article history:

Received 1 September 2015

Accepted 2 December 2015

Available online 21 December 2015

Keywords:

Heterogeneous catalysis

Supported metal nanoparticles

Graphene as support

Graphene supported metal nanoparticles

ABSTRACT

The catalytic activity of metal nanoparticles (MNPs) is highly dependent on the nature of the support. In addition to the role of particle size stabilization in decreasing the spontaneous growth of small MNPs, the main role of the support is to cooperate by providing efficient pathways that lead to the target product. Thus, the necessary requirements for supports include a large surface area, strong metal–support interaction, and the presence of active sites that participate in the reaction mechanism. Active carbons as well as organic polymers and large surface area inorganic metal oxides are typical insoluble solids that are used frequently as supports. Furthermore, the recent availability of suspensions of graphene oxide (GO), reduced GO, and other graphene-based materials (Gs) has provided new opportunities for the development of supported MNPs as catalysts. As supports, Gs combine several useful properties that are not encountered in classical solid supports. Gs comprise sheets that are a single carbon atom in thickness, which approaches the physical limit for a two-dimensional (2D) surface in which MNPs can be deposited. Therefore, Gs are among the solids with the highest possible surface area and due to their single layer morphology, they are readily dispersed in a liquid phase with the appearance of homogeneous catalyst, but they are easily recovered by filtration or centrifugation. In addition, Gs may cooperate with the catalytic cycle involving MNPs in at least four distinctive ways: (i) by strong adsorption of the substrates and reagents near the MNP; (ii) via $d-\pi$ metal support interaction, which influences the electron density of the MNP; (iii) promoting substrate reactivity by giving or withdrawing the electron density from the substrate; and (iv) by making specific catalytic sites available on the G nanosheet due to defects, oxygenated functional groups, or the presence of dopants. This review highlights the specific features derived from the morphology and characteristics of Gs, as well as the different catalytic behaviors of G-supported MNPs compared with related catalysts. One of the aims of this review is to provide a reference to indicate best practices as well as suggesting benchmark reactions to evaluate the catalytic activity of different materials. Considering the growth in the use of G as supports and the unique features obtained by employing 2D Gs as supports for MNPs, the present review has implications in the fields of catalysis, biocatalysis, and material science.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction and scope of the review

A considerable number of heterogeneous catalysts are based on noble metals [1–8] or metal oxides [9] supported on large surface area materials, which should disperse the active sites to avoid the aggregation of particles, thereby yielding stable heterogeneous catalysts. In addition to the large surface area inorganic oxides, and particularly amorphous and porous silicas [10–15], carbonaceous supports are frequently the preferred materials for adsorbing active metals due to their widespread availability, large surface area, and the possibility of controlling the surfaces of these carbons by introducing or removing oxygenated functional groups [16–18]. In this context, in addition to active carbons (ACs) and amorphous carbons, novel carbon nanoforms have been increasingly attracting attention due to their use as supports [19–21]. In the present review, we focus on the use of graphene-based materials (Gs) as supports for noble metal and metal oxide nanoparticles (NPs) in the preparation of heterogeneous or pseudo-homogeneous catalysts. The term pseudo-homogeneous refers to the fact that the solid catalyst can be dispersed persistently in a liquid phase to obtain the appearance of a homogeneous catalyst, but it can still be recovered easily from the reaction mixture by filtration or centrifugation, and eventually reused in consecutive runs. Since 2010, the number of studies describing the use of noble metal or metal oxide NPs supported on G as a catalyst has increased exponentially, mainly because some of the unique features of G render this carbon nanoform highly appropriate as a support of metal nanoparticles (MNPs).

In particular, G comprises a one atom-thick infinite two-dimensional (2D) layer of sp^2 carbons with a hexagonal arrangement, which represents the physical limit of the thickness for a 2D surface, and thus G suspensions have among the largest possible surface area for a suspended material [22–26]. It has been estimated that the theoretical surface area of G is around $2600\text{ m}^2\text{ g}^{-1}$ [27], which is much higher than that of other forms of carbon as well as many other inorganic materials.

In addition to ideal G, other type of derivatives, particularly graphene oxide (GO) and reduced GO (rGO), also possess G with a 2D morphology, high surface area, and the possibility of establishing strong interactions with adsorbates [28]. In particular, GO is suitable for the adsorption of metal oxide NPs, where it can even share some oxygen atoms between two components, which can form part of the inorganic lattice simultaneously while being bonded to the GO or rGO sheet [20,29]. GO contains about 40% oxygen, whereas the oxygen content in rGO is typically lower than 10%. Oxygenated functionalities include carboxylic acid groups, ketones, ethers, and hydroxyls, which can be differentiated and quantified by deconvolution of the C1s peak in X-ray photoelectron spectroscopy (XPS), or by thermoprogrammed desorption coupled with mass spectrometry (TPD-MS). In XPS, the shape and width of the experimental C1s peak can be fitted to individual components in the correct proportion, which correspond to graphenic carbon (sp^2 carbon surrounded by sp^2 carbons) at a binding energy of 284.5 eV, carbon bonded to one oxygen at 286.5 eV, and carboxylic acid carbon at 288 eV. In addition, during TPD-MS, heating of the oxygen-containing G allows the detection of CO_2 derived from the decomposition of carboxylic acid groups, esters, lactones, and anhydrides, which at a higher temperature is followed by the evolution of CO derived from quinone-like groups and hydroxyls.

This review is organized according to the reaction type, including oxidation, reduction, coupling, hydrogen release/storage, and miscellaneous reactions. The use of Gs and doped Gs as electrocatalysts [30–35], photocatalysts [34,36–42], or energy applications [43–45] has been reviewed previously and the reader is referred to existing references for full coverage of these areas. In the present review, we focus on catalytic thermal reactions. When describing the state-of-the-art, we emphasize the reaction mechanism and understanding the origin of the catalytic activity by highlighting the uniqueness of Gs as supports that contribute to the catalytic activity. In the final section, we summarize the main results according to the current state-of-the-art by emphasizing the most important

Download English Version:

<https://daneshyari.com/en/article/1299237>

Download Persian Version:

<https://daneshyari.com/article/1299237>

[Daneshyari.com](https://daneshyari.com)