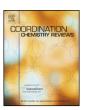


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Review

Metal nanoparticles supported on two-dimensional graphenes as heterogeneous catalysts



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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 Gsupported 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.

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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

In particular, G comprises a one atom-thick infinite two-dimensional (2D) layer of $\rm sp^2$ 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 $2600 \, {\rm m^2 \, g^{-1}}$ [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 (sp² carbon surrounded by sp² 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 CO2 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

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