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Full Length Article

Hydrophobic and hydrophilic nanosheet catalysts with high catalytic activity and recycling stability through control of the outermost ligand

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ABSTRACT

In this study, we introduce hydrophobic and hydrophilic graphene oxide nanosheet (GON) catalysts prepared by consecutive ligand replacement of hydrophobically stabilized magnetic and catalytic nanoparticles (NPs); it exhibits high catalytic activity, fast magnetic response, and good dispersion in both nonpolar and aqueous media, allowing high loading amount of magnetic and catalytic NPs onto GON sheets. More specifically, these GON catalysts showed a high product yield of 66–99% and notable recyclability (93% of the initial product yield after 10 reaction cycles) in a Suzuki–Miyaura reaction in nonpolar media, outperforming the performance of the conventional hydrophilic GON catalysts. Additional coating of a hydrophilic layer onto GON catalysts also showed the notable performance (product yield ~99%) in catalytic reactions performed in aqueous media. Given that ligand-controlled catalytic NPs adsorbed onto 2D nanosheets can be used as hydrophobic and hydrophilic stabilizers as well as catalysts, our approach can provide a tool for developing and designing 2D-nanosheet catalysts with high performance in nonpolar and polar media.

1. Introduction

Metal nanoparticle (NP)-based catalysts have been widely used in a number of chemical reaction-related processes such as photocatalysts or the synthesis of fine chemicals (including intermediates or pharmaceutical products), and electrochemical applications owing to their high surface-to-volume ratio and unusual active sites for better catalytic performance [1–6]. Important parameters for the preparation of high-performance NP catalysts are uniform and stable immobilization of well-defined active NPs on solid substrates with a large surface area and high dispersion of the formed catalyst-supported substrates in desired reaction media. More specifically, because the catalytic reaction of noble metals such as palladium (Pd) in the heterogeneous or semi-heterogeneous catalysis for carbon–carbon (C—C) coupling reactions occurs almost entirely on the particle surface [7–10], a high dispersion of catalytic NPs in the reaction media is required to enhance the catalytic activity. However, NPs without appropriate ligands easily aggregate in aqueous or organic reaction media, reducing their catalytic activity [11,12].

As an alternative, a number of approaches have been developed for the preparation of catalytic NPs with stable immobilization on various solid supports, including carbon-based materials [13–25]. In particular, graphene oxide nanosheets (GONs) have drawn considerable attention owing to their enormous surface area (2630 $m^2 g^{-1}$) [23–25]. For example, most hydrophilic Pd NP-supported GONs (prepared by the direct reduction of Pd ions or by electrostatic assembly) exhibit high catalytic activity in hydrophilic reaction media (*i.e.,* water and/or water/alcohol mixture) but not in nonpolar media because of their poor dispersion stability and stacking phenomenon [26,27]. Pd NP-supported GONs showed high catalytic activity (product yield ~99%) for Suzuki–Miyaura reaction in water or methanol/water mixture [28,29]. However, the product yield in nonpolar media was in the range ~5–69%. Although highly dispersible GON sheets can be prepared in nonpolar media by introducing organic moieties with long alkyl chains onto the surface of the GON sheet [30,31], the resulting GON sheets had no interaction with the surface of the hydrophilic or hydrophobic catalytic NPs. Thus, the 2D-sheet catalysts, such as GON sheet/catalytic nanocomposites have mainly been prepared *via* metal ion reduction or electrostatic assembly that can induce uniform dispersion in only aqueous or water/alcohol mixture media rather than organic media. In this case, the packing density (or loading amount) of catalytic NPs on hydrophilic GONs is limited to the level where the NPs decorate the surface. As a result, a substantial portion of the large surface area remains inactive or bare. Therefore, interface control of catalytic NPs and GONs is strongly required for the development

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