



More than just a support: Graphene as a solid-state ligand for palladium-catalyzed cross-coupling reactions

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ABSTRACT

While the primary role of supports in catalysis has been to anchor metal particles to prevent sintering, supports can also activate catalytic processes. We report computational and experimental results that provide a fundamental understanding of how a graphene support may activate both oxidative and reductive reaction steps in the catalytic cycle of Suzuki-Miyaura palladium-catalyzed cross-coupling reactions. Theoretical investigations reveal that the high catalytic activity is linked to the ability of a graphene support to act as both an efficient charge donor and acceptor in oxidation and reduction reaction steps. We compare the activation energy and turn over frequency for a series of supported and homogeneous catalysts and find that exposing palladium-graphene to defect inducing microwave radiation results in dramatically lower activation energies and higher turnover frequencies. These results explain why a defected graphene support may catalyze reaction steps that require both charge donation, and charge acceptance.

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1. Introduction

Palladium-catalyzed cross-coupling reactions are of strategic importance in the assembly of highly functionalized organic molecules [1–3]. These reactions are typically performed under homogeneous conditions, utilizing ligands to enhance activity and selectivity and are extensively used in the assembly of active pharmaceutical ingredients (API). For these applications, residual metal contamination in the reaction product is a major issue [4,5]. Furthermore, the inability to recycle the metal as well as the ligand represents a significant cost component in API applications. Efforts to address these issues have led to the evaluation of palladium metal clusters with a wide range of traditional catalyst support systems employing a variety of synthetic techniques [4,6–10]. However, for supported catalysts to be effective, the metal must be highly active, and strongly bound to the support in order to minimize metal leaching and maximize recyclability [4,11–13]. Furthermore, a vigorous debate exists over whether these supported Pd species act through a truly heterogeneous process, [4,14,15] or via a homogeneous process involving leached low-coordination Pd in solution promoted by salt [6,16] or oxidative addition [9]. The lack of a fundamental understanding of the rela-

tionship between the properties of the nanoparticle, the support, and the catalytic activity has hindered the development of high performance supported catalysts [6,10,17–23].

The Suzuki reaction follows a three-step pathway of oxidative addition, transmetalation, and reductive elimination [4,7,8]. The reaction benefits from the catalyst acting as a charge donor in the oxidative addition and transmetalation step and as a charge acceptor in the transmetalation and reductive elimination step [24]. In homogeneous catalysts electron donating ligands such as phosphines activate the oxidative addition step, [24] while the oxidation of the Pd atom to Pd(II) then allows the catalyst to become an effective electron acceptor activating the reductive elimination step. If a cluster or nanoparticle is oxidized, the charge will be delocalized over the particle, so the cluster's ability to accept charge will not be significantly enhanced. This is a critical liability in the catalysis of nanoparticles and supported clusters. Many supports are unlikely to enhance both oxidative and reductive reaction steps, [25] however a conductive support may readily both accept and donate charge. Graphene is a conductive support [26] that possesses this capability to activate all three reaction steps and has been shown to demonstrate remarkable catalytic activity in Suzuki reactions [27–30].

In this work, we have performed a synergistic study combining kinetic experiments on various palladium-based catalysts and first-principles theory to determine the activation energy in each step of the catalytic cycle of Suzuki reaction for both free and sup-

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ported Pd species. The effects of the support, active site structure, Pd cluster size, and the electron-rich ligands have also been examined. In particular, we demonstrate that a catalyst consisting of a weakly bound Pd nanoparticle to graphene support exhibits relatively low catalytic activity. When both the Pd precursors and graphene are reduced or partially reduced through microwave irradiation the support provides stronger interaction between the metal particle and support due to the formation of defects in the graphene support [31]. Furthermore, leaching is reduced, the activation energy is drastically decreased, and the reaction rates are significantly increased.

2. Methods and materials

2.1. Typical procedure for Suzuki reaction

4-bromobenzoic acid (64 mg, 0.32 mmol, 1 eq.) was dissolved in a mixture of 4 mL H₂O–EtOH (1:1) and placed in a 10 mL vial. Phenylboronic acid (47 mg, 0.382 mmol, 1.2 eq.), potassium carbonate (133 mg, 0.96 mmol, 3 eq.) was then added to the solution. 0.5% Pd catalyst was then added, the tube was sealed, stirred and heated at 80 °C for 10 min. After the reaction, the mixture was diluted with 10 mL of EtOH and tested in GCMS/HPLC versus internal standard.

2.2. Hydrazine and microwave irradiation Co-reduction (CO) method (Pd/G CO (MW))

For the preparation of Pd on graphene catalysts, 200 mL of deionized water (18.2 MΩ cm), 90 mg of graphene oxide, and 200 μL of palladium nitrate were mixed by ultrasonication at 300 W for 20 min. Then the mixture was stirred for 3 h to allow Pd cation exchange with the acidic functional groups in the GO. Finally, 400 μL of hydrazine was slowly added under stirring and subsequently the solution was irradiated for 2 min in a microwave oven (Emerson MW8119SB) at full power (1000 W), 2.45 GHz. Once the mixture was irradiated, the product was washed and dried overnight *in vacuo* at 80 °C. The resulting catalyst is named Pd/G CO (MW).

2.3. Strong electrostatic adsorption (SEA) method following by hydrogen reduction (Pd/G SEA-H)

For the synthesis of palladium on graphene, a 225 ppm H₂PdCl₄ solution was first made by dissolving 125 mg of PdCl₂ in 0.333 L H₂O and 328.6 μL of 12 M HCl (5.6 M excess). The solution pH was adjusted to pH = 3.25 with diluted aqueous ammonia solution and a 5 mL initial aliquot was taken for inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of Pd content. Next, 1 g of graphene oxide was added to the solution and shaken at 100 rpm on an orbital shaker for 1 h to allow for electrostatic adsorption of PdCl₄²⁻. After shaking for 1 h, a second 5 mL aliquot was taken and 0.2 μm syringe filtered for ICP-OES. The solution was next vacuum filtered, dried, and then reduced in a tube furnace at 180 °C in the presence of H₂ flow. The resulting catalyst is termed Pd/G SEA-H.

2.4. Solventless microwave treatment of Pd/G SEA catalyst (Pd/G SEA-MW)

200 mg Pd/SEA catalyst were placed in a 10 mL tube. The tube was then heated in a CEM microwave reactor at 135 °C for 10 min with magnetic stirring to produce the final Pd/G SEA-MW catalyst. The difference of Pd concentration between before and after

microwave heated, measured by ICP-OES, was used to calculate the Pd wt% of the resulting Pd/G SEA-MW catalyst.

2.5. Kinetic evaluation of Suzuki reaction

Bromobenzoic acid (50 mg, 0.25 mmol, 1 eq.) was dissolved in a mixture of 4 mL H₂O:EtOH (1:1) and placed in a 10 mL vial. Phenylboronic acid (33 mg, 0.3 mmol, 1.2 eq.), potassium carbonate (103 mg, 0.75 mmol, 3 eq.) was then added to the solution. 0.5% Pd catalyst, homogeneous or heterogeneous, was then added, the tube was sealed, stirred and heated in a water bath (at 25 °C, 35 °C, 55 °C, 65 °C and 80 °C respectively). A small aliquot of the reaction mix was tested by HPLC at reaction time 1, 3, 5, 10, 30 and 60 min.

2.6. TEM

The particle size and particle size distribution of the Pd-based nanoparticles were investigated by transmission electron microscopy (TEM) with a Zeiss Libra 120 Plus at 120 kV. For the TEM grid preparation, a drop of the catalyst was diluted in 2 mL of acetone and sonicated for ~10 min. Then, a 300 mesh Cu/lacey-carbon grid was immersed twice in the diluted suspension and allowed to dry at room temperature. Image J 4.18v software was used to measure particle size of the obtained pictures.

2.7. Theoretical

The theoretical studies used a gradient corrected functional proposed by Perdew et al. [32] The VASP code was used, and the Kohn–Sham orbitals were expanded using a plane wave basis set and the cutoff was set to 400 eV [33]. The projector-augmented wave method was used to treat electron–ion interactions. Van der Waals correction (DFT-D2) was applied [34]. A dipole correction was incorporated along the z-axis of the slab, and a Gamma point is used for Brillouin zone integration. Since small Pd_n clusters carry magnetic moments, various spin states were investigated to determine the ground state. Bader charges were used to determine the charge of the individual atoms. Nudge elastic band method was applied to optimize the reaction pathway.

3. Results

To understand the effect of particle size and the particle–support interactions on the catalytic activity, Pd nanoparticles supported on graphene oxide were synthesized by three different methods: (1) graphene oxide impregnated with Pd precursor followed by hydrazine and microwave heating co-reduction (Pd/G CO(MW)), [28,29] (2) Strong Electrostatic Adsorption (SEA) [35] of Pd precursor on graphene oxide followed by hydrogen reduction (Pd/G SEA-H) in a tube furnace, and (3) SEA followed by solventless microwave heating reduction (Pd/G SEA-MW). In the CO and SEA-MW methods, microwave irradiation is used to induce vacancy defect sites that more strongly anchor Pd nanoparticles [36]. The SEA-H method immobilizes the cationic Pd precursors to deprotonated oxygen functional groups and results in uniform Pd nanoparticles, but no vacancy defects are formed. TEM images of the resulting catalysts are shown in Fig. 1. An isolated vacancy defect site, a Pd nanoparticle in a vacancy defect site, as well as a Pd nanoparticle embedded in the graphene support were directly observed by TEM for the Pd/G SEA-MW catalyst (S2), confirming that the microwave irradiation changes the metal–support interaction.

These three supported catalysts and a commercially available supported catalyst were evaluated along with two homogeneous Pd-based catalysts. For each catalyst system, the activation energy

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