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SUPPORTING INFORMATION

Palladium nanoparticles supported on graphene as catalyst for the dehydrogenative coupling of hydrosilanes and amines.

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Pd NPs supported over G



Figure SI1. TEM images of Pd NPs on G where the plane lattice corresponding to Pd NPs can be seen and the spatial distance between different planes measured (b), (c) SAED image focused on a Pd NP showing the presence of several domains and (d) the RAMAN spectra of Pd/G catalyst.

Preparation of Pd/NH₂G.

Graphene oxide was obtained starting from commercial graphite using the Hummers oxidation with an excess of KMnO₄ in NaNO₃/H₂SO4 followed by sonication in water. Graphene oxide was purified by a series of washings and centrifugation cycles. The resulting graphene oxide was suspended in aqueous ammonia and heated at 60 °C for 4 h. After amination NH₂G was washed by redispersion in milliQ water-centrifugation cycles. Pd NPs obtained by the polyol method using K₂PdCl₄ as precursor and ethylenglycol at 140 °C as reducing agent was deposited on aminated graphene.



Figure SI2. TEM images and the Pd NP size distribution for Pd/NH₂G.

Pd NPs supported on multiwall carbon nanotubes (MWCNTs)

Commercial MWCNTs were submitted to purification and pretreatment by adding a sample (150 mg) to HNO₃ (75 mL, 3 M) in a flask. The reaction mixture was stirred at 120 °C for 12 h under reflux. Finally, the solid was collected by filtration, washed until pH 7 and the sample dried by lyophilisation. Subsequently the pretreated MWCNTs were shortened in length by adding a purified MWCNT sample (150 mg) to an acid mixture (concentrated H_2SO_4 6 mL and concentrated HNO₃ 2 mL) in H_2O (20 mL). The mixture was sonicated at 60 °C for 1 h. The solid was washed with water until pH 7 and the H_2O was removed by lyophilization.

Pd NPs deposition.

Treated MWCNTs (100 mg) were added to ethylene glycol (40 mL) and were sonicated for 20 min. $Pd(NO_3)_2$ (11.7 mg) was added to the reaction mixture and the suspension was stirred at 80 °C for 4.5 h. The solid was centrifuged 4 times with acetone and 2 more with H₂O. Finally, the H₂O was removed by lyophilization.





Figure SI3. TEM images and the Pd NP size distribution for Pd-MWCNT.

Pd NPs supported on diamond nanoparticles.

Fenton diamond purification of commercial diamond NPs.

Commercial diamond (0.5 g) was added with H_2O_2 (150 mL) in a flask and, the reaction mixture was sonicated. To this mixture, a solution with FeSO₄ (2 g) in H₂O and cc H₂SO₄ was added. 1 mL of the solution was added over the diamond suspension. Caution the temperature should be controlled because the reaction is very exothermic. When the reaction is finished, the reaction mixture was allow to decant for one night. The liquid is removed and the solid washed with acid water to remove iron from D NPs. Finally, the solid was washed with H₂O until pH 7. The H₂O was removed by liofilization. Dry samples of purified D NPs were reduced with H₂ at 500°C for 6 h.

Pd NPs deposition.

Reduced diamond nanoparticles (50 mg) were placed in a flask with ethylene glycol (40 mL) and sonicated for 20 min. $Pd(NO_3)_2$ (5.8 mg) was added to the reaction mixture and was stirred at 80 °C for 4.5 h. The solid was centrifuged 4 times with acetone and 2 more with H₂O. Finally, the H₂O was removed by liofilization.





Figure SI4. TEM images and the Pd NP size distribution for Pd-DH.

General Procedure for Palladium-Catalyzed Dehydrogenative silylation of amines

The catalyst (0.05 mmol%) was placed in an ampule equipped with a magnetic bar. The amine (10 mmol) was added under a nitrogen atmosphere and the ampule was sonicated for 1h. Then, hydrosilane (5 mmol) and dodecane (internal standard) were added to the ampule and the reactor sealed. The reaction mixture was stirred at 50 or 120 °C

(depending on the amine boil point) in an oil bath. At the end of the reaction, the reaction mixture was cooled to room temperature, diluted with anhydrous toluene and filtered. The clean solution was evaporated and the residue was purified by distillation under reduced pressure in an oven ball.

PRODUCTS



4-(Dimethylphenylsilyl)morpholine. CAS Registry number 863454-94-8.

RMN de ¹H (400MHz, CDCl₃) δ 7.39-7.36 (m, 2H), 7.19-7.16 (m, 3H), 3.39-3.37 (m, 4H), 2.67-2.65 (m, 4H), 0.17 (s, 6H).

EIMS (m/z,%): 221(M⁺), 206 (M⁺-CH₃), 191 (M⁺,-2·CH₃), 135 (M⁺-C₄H₈NO).



N-Propyl-1,1-dimethyl-1-phenylsilanamine.

RMN de ¹H (400MHz, CDCl₃) δ 7.68-7.60 (m, 2H), 7.43-7.38 (m, 3H), 2.52 (t, 2H, *J*= 7.9), 1.40-1.32 (m, 2H), 0.82-0.79 (m, 3H,) 0.50 (s, 6H).

EIMS (m/z,%): 193 (M⁺), 178 (M⁺-CH₃), 164 (M⁺,-C₂H₅), 135 (M⁺-C₃H₈N).



1,1-Dimethyl-N,1-diphenyl-silamine. CAS Registry Number 13091-06-0.

RMN de ¹H (400MHz, CDCl₃) δ 7.70-7.60 (m, 2H), 7.45-7.30 (m, 3H), 7.15-

7.05 (m, 2H), 6.75-.60 (m, 3H), 2.60 (s, 1H), 3.67 (s, 1H), 0.52 (s, 6H).

EIMS (m/z,%): 227 (M⁺), 215 (M⁺-CH₃), 135 (M⁺,-C₅H₅), 91 (M⁺-C₅H₅N).



4-(Triethylsilyl)morpholine. CAS Registry Number 161192-76-3

RMN de ¹H (400MHz, CDCl₃) δ 3.62-3.60 (m, 4H), 2.82-2.79 (m, 4H), 0.90 (t, 9H, *J* = 7.9), 0.51 (c, 6H, *J*= 8.0).

EIMS (m/z,%): 201 (M⁺), 172 (M⁺-C₂H₅), 144 (M⁺,-2·C₅H₅), 114 (M⁺-3·C₂H₅).



1,1,1-Triethyl-N-propylsilanamine. CAS Registry Number 17887-11-5.

RMN de ¹H (400MHz, CDCl₃) δ 2.65 (t, 2H, *J* = 8.0), 1.55-1.46 (m, 4H), 0.90-0.84 (m, 12H), 0.50 (c, 6H, *J*= 8.1).

EIMS (m/z,%): 173 (M⁺), 144 (M⁺-C₂H₅), 116 (M⁺, -2·C₅H₅), 87 (M⁺-3·C₂H₅).



N-(Triethylsilyl)benzenamine. CAS Registry Number 18106-48-4

RMN de ¹H (400MHz, CDCl₃) δ 7.19-7.14 (m, 2H), 7.10-7.07 (m, 3H), 2.59 (s, 1H), 0.86 (t, 9H, *J*= 7.19), 0.44 (c, 6H, *J* = 7.8).

EIMS (m/z,%): 207 (M⁺), 178 (M⁺-C₂H₅), 150 (M⁺,-2·C₅H₅), 122 (M⁺-3·C₂H₅).



1,1-diphenyl-N,N-dipropylsilanediamine. CAS Registry Number 18055-66-8.

RMN de ¹H (400MHz, CDCl₃) δ 7.65-7.42 (m, 4H), 7.38-7.20 (m, 6H), 2.52 (t, 4H, *J* = 7.9), 1.60 (bs, 2H) 1.34 (m, 4H,), 0.81 (t, 6H, *J* = 7.8).

EIMS (m/z,%): 298 (M⁺), 269 (M⁺-C₂H₅), 240 (M⁺-NHC₃H₇), 212 (M⁺,-NHC₃H₇, C₂H₅), 183 (M⁺-2·NHC₃H₇).

N-(Triethylsilyl)-O-(Triethylsilyl)acetamide.

RMN de ¹H (400MHz, CDCl₃) δ 1.89 (s, 3H), 0.87 (t, 18H, *J* =7.8), 0.65 (c, 12H, *J*=7.9).

EIMS (m/z,%): 258 (M⁺-C₂H₅), 230 (M⁺-2·C₂H₅), 172 (M⁺,- Si·(C₂H₅)₃) 144 (M⁺,- Si·(C₂H₅)₃, -C₂H₅).