SUPPORTING INFORMATION

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

Juan F. Blandez, Ivan Esteve, Ana Primo, Mercedes Alvaro, Hermenegildo Garcia
Instituto Universitario de Tecnología Química CSIC-UPV and Departamento de Química, Univ. Politécnica de Valencia, Av de los Naranjos s/n, 46022 Valencia, Spain.
E-mail: hgarcia@qim.upv.es

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 KMnO$_4$ in NaN$_3$/H$_2$SO$_4$ 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 NH$_2$G was washed by redispersion in milliQ water-centrifugation cycles. Pd NPs obtained by the polyol method using K$_2$PdCl$_4$ as precursor and ethyleneglycol at 140 °C as reducing agent was deposited on aminated graphene.

![Figure SI2. TEM images and the Pd NP size distribution for Pd/NH$_2$G.](image)

**Pd NPs supported on multiwall carbon nanotubes (MWCNTs)**

Commercial MWCNTs were submitted to purification and pretreatment by adding a sample (150 mg) to HNO$_3$ (75 mL, 3 M) in a flask. The reaction mixture was stirred at 120 ºC 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$_2$SO$_4$ 6 mL and concentrated HNO$_3$ 2 mL) in H$_2$O (20 mL). The mixture was sonicated at 60 ºC for 1 h. The solid was washed with water until pH 7 and the H$_2$O 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 H$_2$O. Finally, the H$_2$O was removed by lyophilization.
Pd NPs supported on diamond nanoparticles.

Fenton diamond purification of commercial diamond NPs.

Commercial diamond (0.5 g) was added with H$_2$O$_2$ (150 mL) in a flask and, the reaction mixture was sonicated. To this mixture, a solution with FeSO$_4$ (2 g) in H$_2$O and cc H$_2$SO$_4$ 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 H$_2$O until pH 7. The H$_2$O was removed by liofilization. Dry samples of purified D NPs were reduced with H$_2$ 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 H$_2$O. Finally, the H$_2$O was removed by liofilization.
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 $^1$H (400MHz, CDCl$_3$) $\delta$ 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$^+$-CH$_3$), 191 (M$^+$,-2·CH$_3$), 135 (M$^+$-C$_4$H$_8$NO).

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

RMN de $^1$H (400MHz, CDCl$_3$) $\delta$ 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$^+$-CH$_3$), 164 (M$^+$,-C$_2$H$_5$), 135 (M$^+$-C$_3$H$_8$N).
1,1-Dimethyl-N,1-diphenyl-silamine. CAS Registry Number 13091-06-0.

RMN de $^1$H (400MHz, CDCl$_3$) 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$^+$-CH$_3$), 135 (M$^+$-C$_5$H$_5$N), 91 (M$^+$-C$_3$H$_3$N).

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

RMN de $^1$H (400MHz, CDCl$_3$) 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$^+$-C$_2$H$_5$), 144 (M$^+$-2·C$_3$H$_5$), 114 (M$^+$-3·C$_2$H$_5$).

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

RMN de $^1$H (400MHz, CDCl$_3$) 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$^+$-C$_2$H$_5$), 116 (M$^+$-2·C$_3$H$_5$), 87 (M$^+$-3·C$_2$H$_5$).
**N-(Triethylsilyl)benzenamine.** CAS Registry Number 18106-48-4

RMN de $^1$H (400MHz, CDCl$_3$) 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$^+$-C$_2$H$_5$), 150 (M$^+$-2·C$_2$H$_5$), 122 (M$^+$-3·C$_2$H$_5$).

![N-(Triethylsilyl)benzenamine](image)

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

RMN de $^1$H (400MHz, CDCl$_3$) 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$^+$-C$_2$H$_5$), 240 (M$^+$-NHC$_3$H$_7$), 212 (M$^+$-NHC$_3$H$_7$, C$_2$H$_5$), 183 (M$^+$-2·NHC$_3$H$_7$).

![1,1-diphenyl-N,N-dipropylsilanediamine](image)

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

RMN de $^1$H (400MHz, CDCl$_3$) δ 1.89 (s, 3H), 0.87 (t, 18H, $J$ =7.8), 0.65 (c, 12H, $J$=7.9).

EIMS (m/z, %): 258 (M$^+$-C$_2$H$_5$), 230 (M$^+$-2·C$_2$H$_5$), 172 (M$^+$- Si·(C$_2$H$_5$)$_3$) 144 (M$^+$- Si·(C$_2$H$_5$)$_3$, -C$_2$H$_5$).

![N-(Triethylsilyl)-O-(Triethylsilyl)acetamide](image)