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

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¹⁰ Palladium nanoparticles (Pd NPs) have been supported on undopped and N- or B-doped graphenes (Gs) and these materials have been used as catalysts for the dehydrogenative coupling of hydrosilanes and amines to form silazanes. Working under optimal conditions, a conversion over 99 % and selectivity of 84 % were achieved for the reaction of dimethylphenylsilane with morpholine. In contrast, copper (Cu NPs) or nickel nanoparticles (Ni NPs) supported on G did not promote the formation of the corresponding

¹⁵ Si-N coupling product. It was found that Pd/G performed better for this coupling than analogous catalysts in where Pd NPs were supported in active carbon, multiwall carbon nanotubes or diamond NPs. Pd/G as catalyst has a wide substrate scope, including aliphatic and aromatic amines and mono or dihydrosilanes. Pd/G undergoes a gradual deactivation due to the growth and partial agglomeration of Pd NPs and aggregation of the G sheets, as observed by TEM.

20 1. Introduction

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Due to the unique properties derived from its 2D morphology and the one-atom thickness, graphene (G) offer unique properties as support for metal NPs.¹⁻⁷ The interest of G and related material as supports in catalysis derives from its large specific surface area ²⁵ that can be as large as 2500 m²×g⁻¹,⁸ as well as from the strength of the interaction with the supported metal NPs arising from the overlap of the extended π orbital of G with the d orbitals of transition metal atoms at the interface of G and the metal NP. G is constituted by one atom thick layer of sp² carbons in hexagonal

- ³⁰ arrangement and, therefore, the use of this type of material as support represents the physical limit of miniaturization corresponding ideally to the minimum thickness for surface area.⁹⁻¹¹ In addition, the properties of G as support can be modified and its electronic effects tuned by the presence of
- ³⁵ defects, oxygenated functional groups and heteroatoms.¹²⁻¹⁷ Theoretical calculations at the DFT level with G models with one carbon atom vacancy interacting with transitions metals has shown that this type of defect characterized by dangling bonds on G is particularly suited to interact with metal atoms.¹⁸ Similar
- ⁴⁰ type of computational calculations also indicate that heteroatoms on the G sheet can stabilize metal NPs. The so far reported data in the literature support that G is a unique material offering as support many opportunities to enhance the catalytic activity of metal NPs.

⁴⁵ In this context, the present manuscript reports the catalytic activity of doped G supported Pd NPs for the dehydrogenative coupling of hydrosilanes and amines (Eq. 1).

$$\begin{array}{cccc} R^{1} & H \\ I & + \end{array} \begin{array}{c} N - R^{4} & \xrightarrow{\text{Catalyst}} & R_{2}^{-} Si - N - R_{4} + H_{2} & (\text{Eq. 1}) \\ R^{2} & Si \\ R^{3} & & R_{3}^{2} \end{array}$$

This reaction between hydrosilanes and amines has been reported 50 in the literature with homogeneous catalysts using mainly Pd complexes.^{19, 20} Related to the dehydrogenative coupling of hydrosilanes and amines, the analogous reaction between hydrosilanes and alcohols has been recently reported to be performed using heterogeneous catalysts.²¹ In particular, it has 55 been found that supported Au NPs can efficiently act as heterogeneous catalysts for the reaction between hydrosilanes and alcohols, giving rise to the corresponding siloxane. Considering these precedents, it could also be that the coupling of hydrosilanes and amines can equally be promoted by supported 60 metal NPs, Pd NPs being an obvious choice considering the known catalytic activity of Pd complexes for this reaction.^{19, 20} The commercial interest of the resulting silazanes stems from their applications as silylating agents 22-25 and for coating of material surfaces.

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2. Results and Discussion

A series of different Gs were prepared and used as supports of metals NPs. These materials were obtained, as reported, by pyrolysis under inert atmosphere of alginate or chitosan ⁵ conveniently modified or not by boric acid.²⁶⁻²⁸ The resulting carbonaceous residues after pyrolysis can be exfoliated without the need of additional chemical oxidation to form single and few layer G suspensions in different solvents. This G material was used as support of metal NPs that were prepared by the polyol ¹⁰ method, using ethyleneglycol as reducing agent.²⁹ Scheme 1 illustrates the process followed for the synthesis of metal NPs supported on Gs.



Scheme 1 Procedure employed for the preparation of the G materials ¹⁵ under study. Corresponding characterization data are provided in the supporting information. i) pyrolysis at 900 °C under Ar, ii) sonication for 1 h, iii) reduction for 24 h in reflux at 120 °C.

Specifically the doping content and the distributions of the doped ²⁰ element in two different sites were determined by quantitative XPS analysis.²⁶ The layer morphology and the hexagonal arrangement of the C atoms were established by high resolution TEM imaging together with selected area electron diffraction. Fig. 1 shows representative images of the samples to illustrate the ²⁵ morphology of G and the particle size distribution of Pd NPs.



Fig.1 a) and b) TEM images of Pd/G at different magnifications. The inset shows the Pd particle size distribution. c) AFM image of a layer of exfoliated Pd/G catalyst and d) its section profile.

- ³⁰ Fig. S1 in the supporting information also shows a high-resolution image of Pd NPs in which the expected lattice spacing of 0.27 nm corresponding to the (1.1.1) facets of Pd can be clearly observed, as well as the different orientations of the planes and the existence of nanodomains. Analysis of a ³⁵ statistically relevant number of these Pd shows that these metal NPs do not present a preferential facet. Supporting information provides the selected area electron diffraction pattern of one of these Pd NPs.
- Although TEM shows the expected wrinkles and light contrast 40 expected for single layer G, this technique is generally not considered as conclusive with respect to the single layer morphology of Gs. The single and few layers configuration of the suspended G platelets is more safely determined by AFM measurements of the vertical height of a statistically relevant 45 number of G platelets (Fig. 1). The G structure and the presence of defects was established by Raman spectroscopy in where the characteristic graphitic (G) and defect (D) peaks appearing at about 1600 and 1350 cm⁻¹ were observed. In agreement with the predominant single-layer morphology of G, the presence of a ⁵⁰ weak band at about 2690 cm⁻¹ was also observed. A quantitative estimation of the relative importance of defects for the various G samples can be obtained from the relative intensity ratio of the G versus the D bands.³⁰⁻³³ I_D/I_G ratio of 0.84 was measured that is a value notable much lower than those typically reported in the 55 literature for G samples obtained by reduction of graphene oxide^{34, 35} that are about 1.4. This indicates that the G sample used here has lower density of defects. The surface area of G suspended in aqueous solution was estimated by the methylene blue (MB) method.^{36, 37} In these measurements, the amount of 60 MB adsorbed on G is determined by the decrease of the intensity of the visible absorption band of MB upon adsorption on G and removal of MB-G conjugate. The specific surface area was estimated 1550 $m^2 \times g^{-1}$, in the range, but lower, of the theoretical maximum area of completely exfoliated G materials.⁸ Overall, all 65 the available characterization data of the G materials employed in the present study are in agreement with reported literature data that has previously established the formation of undoped or doped G suspensions following the procedure employed in the present study.26

In the initial stage of our work and in order to optimize the reaction conditions and select the most active catalyst, the dehydrogenative coupling of dimethylphenylsilane and morpholine was chosen as model reaction. The influence of the ⁷⁵ reaction at temperature from 60 to 120 °C, as well as the nature of co-solvent and catalyst was studied.



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Table 1 Results of the dehydrogenative coupling of dimethylphenylsilane (1a) and morpholine (2a) in the presence of different catalysts with or without metal NPs supported on G.

$$(1a) (2a) \xrightarrow{Catalyst [0.05 mol%]}{Ar} \xrightarrow{S_1} (3a) (4a)$$

Catalyst		T (°C)	t (h)	Conversion (%) ^b	Selectivity (%) ^b		
1	G	60	24	20	0		
2	Cu/G	60	24	22	0		
3	Cu/(N)G	60	24	7	0		
4	Cu/(B)G	60	24	17	0		
5	Cu/D	60	24	30	0		
6	Ni/G	60	24	6	0		
7	Pd/G	60	3	70	67		
8	-	120	24	0	0		
9	Cu/G	120	24	67	2	4	
10	Pd/G	120	0.5	99	89		
11	G	120	48	47	12		
12	Pd/NH ₂ G	120	3	99	74		
^a Reaction conditions: 1a (5 mmol), 2a (10 mmol), catalyst (0.05 mol%),							

s ^a Reaction conditions: **1a** (5 mmol), **2a** (10 mmol), catalyst (0.05 mol%), Ar atmosphere. ^b Conversion and selectivity were determined by GC using internal standard.

Table 1 summarizes the main results obtained in this screening tests. Gs in the absence of metals NPs (Table 1, entry 11) ¹⁰ catalyses exclusively disiloxane formation, the yield and the selectivity toward the desired product, **3a**, being negligible even after much longer times than those employed later. Also Cu NPs and Ni NPs at metal to substrate molar ratio of 0.05 mol% fail to promote the dehydrogenative coupling. At high temperatures ¹⁵ (120 °C) and long reaction time (24 h), a notable hydrosilane **1a** conversion was observed using Cu/G as catalyst (Table 1, entry 9). However, in spite of the high **1a** conversion, only trace amounts of the desired silazane **3a** was detected under these conditions. This negative result contrasts with the catalytic ²⁰ activity recently found for Cu/G in the analogous dehydrogenative coupling of hydrosilanes with primary alcohols to render alcoxysilanes.³⁷ Apparently the different properties of

and acidity of the hydrogens bonded to the heteroatom should be ²⁵ responsible for this notable difference in the catalytic behavior of Cu/G for these two related reactions. In contrast, Pd containing catalysts promote the Si-N coupling

alcohols and amines in terms of nucleophilicity of the heteroatom

with high selectivity to product 3a at high substrate conversion. It was observed that, at the same Pd loading, the nature of the G and

³⁰ the presence of dopant element plays a certain influence on the catalytic activity. It was found that N-doping was detrimental for the catalytic activity, while the presence of B does not increase the activity with respect to undoped G. Accordingly Pd/G (Table 1, entry 10) is apparently the best choice to promote this

³⁵ coupling. As expected, the reaction temperature played a notable influence on the conversion and selectivity that increased as the temperature increased from 80 to 120 °C (see Table 2, entries 1, 2 and 3).

This influence of temperature on the initial reaction rate has ⁴⁰ allowed us to estimate the activation energy of the process from the slope of the Arrhenius plot of log (k) versus 1/T (Fig. 2).



Fig. 2 Plot of the logarithm of the reaction rate constant (k) vs the inverse of the absolute temperature (T) for the dehydrogenative coupling of dimethylphenylsilane (1a) and morpholine (2a). The inset shows the temporal profile of product formation at 80 °C (\blacklozenge), 100 °C (\blacksquare) and 120 °C (\blacktriangle).

The activation energy (Ea) estimated from the Arrhenius plot (Fig. 2) was 22.9 kJ×mol⁻¹ that is a low Ea value, but in the range ⁵⁰ of those determined for the Cu-catalyzed dehydrogenative coupling of hydrosilane and alcohols.³⁷ Therefore, a suitable reaction temperature was 120 °C. Working at this temperature and a Pd/substrate mol ratio of 0.05 %, full conversion **1a** was obtained in 30 min (Table 1, entry 10).

⁵⁵ With regard to the influence of co-solvents, it was observed that the presence of 1,4-dioxane or toluene (Table 2, entries 4 and 5) is highly detrimental for the catalytic activity that disappear completely when any of these two solvents was present. Thus, reactions were carried out in the absence of co-solvents. The ⁶⁰ morpholine-hydrosilane mol ratio was also optimized. Initially, an amine-hydrosilane mol ratio of 2 was selected, considering that the amine should play the role of reactant and solvent. But also, a 1:1 (Table 2, entry 7) and 1:2 mol ratios between morpholine and hydrosilane (Table 2, entry 8) were evaluated. It ⁶⁵ was found that a decrease in the mol ratio of morpholine leads to a decrease in the yield of the silazane coupling product. Catalysis Science & Technology Accepted Manuse

 Table 2 Optimization of the reaction conditions for the dehydrogenative coupling of 1a and 2a catalyzed by Pd/G.

So	lvent	1a (mmol)	2a (mmol)	T (°C)	t (h)	Convers ion (%) ^b	Selectivit y (%) ^b
1		1	2	80	0.5	28	0
2		1	2	100	0.5	77	7
3		1	2	120	0.5	99	89
4	1,4- Dioxane	1	2	120	24	0	0
5	Toluene	1	2	120	24	0	0
7		1	1	120	0.5	99	70
8		2	1	120	0.5	75	43

^aReaction conditions. Catalyst Pd/G (0.05 mol%), Ar atmosphere. ⁷⁰ ^b Conversion and selectivity were determined by GC using internal standard.

An additional experiment was carried out at 120 °C in the absence of co-solvent and **1b-2a** mol ratio of 1-2, but using ten 75 times lower amount of Pd/G (Pd-1b mol ratio 0.003 mol%). Full **1b** conversion was also achieved in this experiment with very high selectivity to **3d**, reaching a TON of product molecules per

Pd atom of 33,300 although requiring much longer reaction time (24 h).

With the optimal conditions for the model reaction (120 °C, no co-solvent, amine-silane mol ratio 2) the catalytic activity of ⁵ Pd/G was compared to that of other Pd NPs supported in different carbon materials. The results are presented in Table 3.

 Table 3 Catalytic activity of Pd NPs supported on different carbon materials.

Catalyst ^b		talyst ^b	T (°C)	t (h)	Conversion (%) ^c	Selectivity (%) ^b
	1	Pd/G	120	0,5	99	89
	2	Pd/(N)G	120	0,5	84	74
	3	Pd/(B)G	120	0,5	96	87
	4	Pd/C	120	0,5	99	81
	5	Pd/MWCNT	120	0,5	99	84
	6	Pd/DH	120	0,5	92	63

^aReaction conditions: **1a** (5 mmol), **2a** (10 mmol), catalyst (0.05 mol%), ¹⁰ Ar atmosphere. ^bMWCNT: multi-walled carbon nanotubes, DH: hydrogen-treated diamond nanoparticles. ^cConversion and selectivity were determined by GC using internal standard.

Specifically in the present study the catalytic activity of Pd NPs supported on multiwall carbon nanotubes (MWCNTs) and ¹⁵ reduced diamond nanoparticles (DH) was also checked. MWCNTs have many similarities with the structure of G and, as expected, the catalytic activity obtained using MWCNT as support was very similar (Table 3, entry 5), the main difference should derive from the curvature of the G wall forming to the ²⁰ nanotube. In contrast, it has been found that DH offers a highly inert environment to metal NPs, due to the lack of chemical reactivity and presence of functional groups on the diamond surface. In this case **1a** conversion was very similar to that achieved with Pd/G, but the selectivity to the desired product was

- ²⁵ very low (Table 3, entry 6). Besides allotropic carbon forms, active carbons have been favorite supports in catalysis due to the large surface area and high adsorption capacity of these materials. The comparison of catalytic data shows that Pd NPs supported on active carbons (Table 3, entry 4) exhibit also a good performance,
- ³⁰ but with lower yield than that achieved with Pd/G. This comparative study shows the superiority of G as support for this dehydrogenative coupling with respect to other carbon supports. In the literature there are precedents also showing the higher efficiently of supported metals NPs on G compared to other
- ³⁵ related carbons materials.^{37, 38} This better performance has been attributed to the combination of three factors, namely, large surface area of G, strong metal NPs-G interaction that may change the electronic density of the metal atoms at the metal NP-G interface and the presence of an extended π orbital favoring
- ⁴⁰ adsorption of substrates and reagents near the metal NPs.^{38, 39} It can be assumed that the same effects could also operate in the present case.

Stability of Pd/G as catalyst was studied by performing consecutive reuses of the same Pd/G sample and determining the

⁴⁵ time-conversion plots for each run (Fig. 3). After each reaction, the catalyst was recovered by filtration, washed with hexane, dried at the ambient and submitted to another consecutive run. In addition, Pd content in the liquid phase after removal of the catalyst was also determined by ICP analysis to assess the ⁵⁰ possibility of Pd leaching from Pd/G to the liquid phase.



Time (min)

Fig.3 Temporal profiles of 1a conversion after two consecutive uses of the same Pd/G and Pd/G-(NH₂) sample as catalyst. Reaction conditions: ratio between 1a and 2a 1:2, catalyst (0.05 mol%), Ar atmosphere. First sed of Pd/G (→), second used of Pd/G (→), and first used of Pd/G-(NH₂) (→) and second used of Pd/G-(NH₂) (X).

As can be seen in Fig. 3, a gradual decrease in activity was observed upon reuse, particularly between the second and the third use. Analysis of Pd in the liquid phase indicates that only the 0.12 % of the initial Pd has leached from G to the liquid phase and that four times reused Pd/G still contains more than 99 % of the Pd content of the fresh sample. This analytical data indicates that the loss of Pd cannot be the cause of the catalyst deactivation observed in Fig. 3. This negligible percentage of Pd leaching is in favor of a strong Pd/G interfacial interaction. We also performed

- a *hot filtration test* in which the reaction starts in the presence of catalyst, but then the catalyst is removed by filtration while the suspension is still hot at a conversion of about 30% (5 min). As it can be seen in Fig. 4, the reaction stops when Pd/G is removed ⁷⁰ from the reaction mixture. This indicates that there is no
- significant contribution of homogenous catalysis due to the small Pd leaching. These *hot filtration* data are in accordance with the low amount of Pd leaching previously described.



75 Fig.4 Time-conversion plots for the reaction of 1a and 2a without (black) and with hot filtration at 5 min allowing the reaction to continue in the absence of Pd/G.

After four consecutive reuses, Pd/G was characterized by TEM (Fig. 5). Statistical analysis of the particle size distribution shows that after reuse of Pd/G the dimension of Pd NPs is between 3-7 nm. However, these images revealed also the formation during

the course of the reaction of some particles of much bigger size.



Fig.5 TEM images at two different magnifications of Pd/G catalyst after four uses. The inset shows the particle size distribution of Pd NPs.

- ⁵ The appearance of these large agglomerated Pd particles was observed in the almost deactivated catalyst, indicating that particle size increase is, probably, one of the main causes of Pd/G deactivation. Also in some areas the expected 2D morphology of G was not observed, and it seems that some G sheets become ¹⁰ corrugated forming 3D objects. This change in the morphology of
- G should also lead to catalyst deactivation due to the decrease in the surface area of the G layers.

In view of Pd/G catalyst deactivation and Pd NP agglomeration, it is pertinent to comment that the *hot filtration* tests have to be

- ¹⁵ taken cautiously in catalysis by Pd NPs.⁴⁰ Prior work in the field has shown that minor amounts of Pd leached from the solid to the solution during the course of the reaction can be responsible for the observed conversion.⁴⁰ This leached Pd re-deposit on the support, mainly in an inactive, *resting* form upon cooling.⁴⁰ This
- ²⁰ mobilization of Pd species and re-deposition will cause the growth of the average particle size and the gradual inactivation of the catalyst. In this context, it is worth noting that trace amounts of Pd in the ppm level have been detected in solution during catalysis in different types of C-C and C-.X bond formation and ²⁵ considered to be the catalytically active species.⁴⁰

An attempt was made to develop a G supported catalyst with higher reusability. It was reasoned that the presence on G of

amino groups could increase the affinity of Pd NPs for G and this could eventually lead to a reusable G catalyst. To test this ³⁰ possibility a sample of graphene oxide was treated with an

- aqueous NH₃ solution at 60 °C to lead to NH₂G with a N content determined by combustion chemical analysis of 8.1 %. Deposition of Pd NPs on NH₂G leads to a catalyst that also shows a notable catalytic activity for Si-N coupling, although lower than ³⁵ that of Pd/G (Table 1 compare entries 12 and 10). However, in
- spite of the presence of NH_2 groups on G, reuse of Pd/NH_2G also led to a significant degree of deactivation from 99 to 68 % conversion in 3 h and, thus, the catalytic activity of Pd/NH_2G was not further explored.
- ⁴⁰ The scope of Pd/G as catalyst for the coupling of hydrosilanes and amines was expanded by studying the reactivity of other aromatic and aliphatic mono and dihydrosilanes with primary and secondary aliphatic amines, as well as, aniline and acetamide. The results obtained are shown in Table 4 and supporting
- ⁴⁵ information provides spectroscopic data of the resulting silazanes. As it can be seen in Table 4, high conversions respect to the hydrosilane were obtained in all cases with selectivity values toward the expected silazane from good to high.
- Due to the low boiling point, coupling with propylamine (2b) was ⁵⁰ carried out at 50 °C, allowing the reaction to run for much longer time (Table 4, entries 2 and 5), achieving for 1a and triethylsilane (1b) high conversion and selectivity. Diphenylsilane (1c) also undergoes coupling with propylamine and the product for the double coupling could be obtained with very high yields when the
- ⁵⁵ reaction was performed at 120 °C. Aniline (2c) as substrate can also undergo dehydrogenative coupling with 1a and 1b to form the corresponding N-phenylsilazanes 3b and 3c. Even acetamide (4b) can react under the present conditions. In this case, bis-O,N-disilane was the corresponding product observed in moderate ⁶⁰ yield at 120 °C. Bis-O,N-disilane and related derivatives are among the preferred silvlating reagents to perform the
- among the preferred silylating reagents to perform t derivatisation of OH groups in sugars.⁴¹

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Table 4. Activity data for the dehydrogenative coupling of hydrosilanes and amines catalysed by Pd/G.

^a Indicate optimal reaction conditions, ^b The selectivity and the conversion were determined by GC with internal standard.^b The Selectivity and the conversion were determined by ¹H-NMR spectroscopy.

3. Conclusions

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In the present manuscript it has been found that from the various

doped and undoped G, Pd NPs supported on G is a suitable catalyst to promote the dehydrogenative coupling of hydrosilanes ¹⁰ and primary or secondary amines with high conversion and good or high selectivity to the corresponding mono or disilazanes. The reaction takes place even for aromatic amines and acetamide. In contrast, Cu NPs and Ni NPs do not promote this reaction. The use of G as support is advantageous with respect to other forms of

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carbons including active carbons, MWCNTs and DH NPs. Pd/G undergoes a gradual deactivation upon use, the most probable causes being Pd NP agglomeration and aggregation of the G sheets.

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