The final publication is available at

http://dx.doi.org/10.1016/j.jcat.2013.02.019

Additional Information

Supported Palladium Nanoparticles as Heterogeneous Ligand-Free Catalysts for the Hiyama C-C coupling of vinylsilanes and halobenzenes leading to Styrenes

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1. INTRODUCTION

The Heck, Kumada, Negishi, Stille, Suzuki and Hiyama couplings are general reactions to form aromatic compounds.[1-13] Simple styrenes are difficult to be prepared by Heck coupling[14] since the reaction would require the use of unsubstituted ethylene gas as substrate, this making the process impractical. In addition, ethylene exhibits low reactivity.

Styrenes are among the most important monomers to form a large variety of functionalized and crosslinked organic copolymers.[15] This type of macromolecules requires polymerization of vinyl aromatics that cannot be obtained by the Heck reaction. The alternative for the preparation of substituted styrenes that has been employed in the present case is based on the Hiyama[16] coupling that uses vinylsilanes as reagents together with aryl halides and where the key step is cleavage of the C-Si bond (Scheme 1).

Typically, the Hiyama reaction of aryl-halides with vinylsilanes is catalysed in homogenous phase by palladium salts such $PdCl_2$, $Pd(OAc)_2$ and palladium(0) complexes like $Pd(PPh_3)_4$ in the presence of organic ligands and salts as additives to enhance the rate and selectivity.[17, 18] A natural tendency in catalysis is to transform a successful homogenous catalytic process into a heterogeneous catalyzed reaction in where the solid catalyst can be easily separated from the reaction mixture and reused in consecutive batch reactions[19, 20] or employed under continuous flow conditions.[21] Although there are some precedents reporting Pd-grafted periodic mesoporous organosilica[22] and polystyrene-supported palladium[23] catalysts for some Hiyama and Sonogashira coupling. Therefore, it would be of interest to develop heterogeneous palladium catalysts[24-26] for the Hiyama reaction with vinyl silanes leading to styrenes, particularly in the absence of ligands, as it will be the case here.

Scheme 1. Ligand-free Hiyama coupling of aryl halides and vinylsilanes leading to styrenes and other coupling by-products.
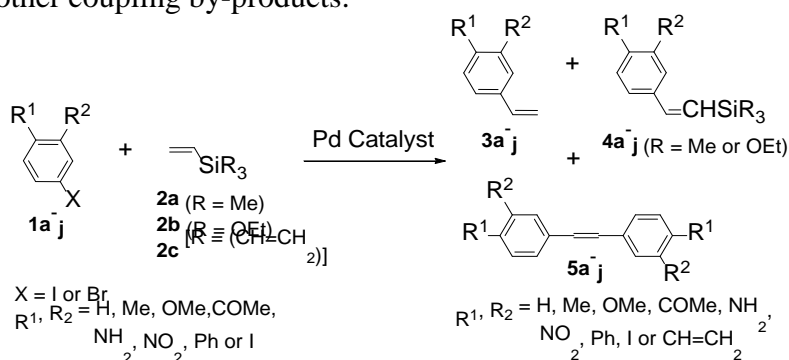
In the present study, we report a novel heterogeneous ligand-free catalyst based on supported palladium nanoparticles to promote Hiyama coupling. Considering the importance of substituted styrenes in polymer chemistry and the difficulty to obtain these monomers by other C-C coupling reactions, our solid palladium catalyst is advantageous since it can promote the Hiyama coupling in the absence of ligand and, in addition, it can be recycled in consecutive runs.

## 2. RESULTS AND DISCUSSION

2.1. Catalysts

In the first stage of our work we prepare a series of palladium catalysts and tested their activity for the process indicated in Scheme 1. As support of palladium NPs we selected active carbon as well as three nanoparticulated metal oxides with acid (TiO_2 or CeO_2) or basic (MgO) nature. These metal oxide-supported palladium catalysts were prepared by impregnation at pH 7 followed by thermal reduction with 1-phenylethanol (see experimental section for details).

The palladium loading of the catalyst was determined by elemental analysis and ranged from 0.8 to 3 wt% depending on the sample. Transmission electron spectroscopy [see images in supporting information (Figs. S1, S2 and S3)] revealed in all cases the presence of palladium NPs with average particle size ranging from 1.9 to 3.5 nm, as indicated in Table S1 in supporting information.

The oxidation state of palladium and the interaction of this metal with the support were evaluated by XP spectroscopy. Figure 1 show selected XP spectra of the palladium $3d_{5/2}$ peaks to illustrate the various proportions between Pd(0) and Pd(II) on a given support. It is worth commenting that the percentage of Pd(0) and Pd(II) changes significantly depending on the catalyst. A summary of XPS data is provided in Table S1 and for details see Fig. S4, S5 and S6 in supporting information.

For the sake of comparison we have also included in our study analogous material in which platinum NPs have been supported on MgO following a similar procedure and leading to a metal loading in the range of those used for the other supported palladium catalysts.

Figure 1. Palladium peaks of the XP spectrum corresponding to the $3d_{5/2}$ core levels measured for a sample of 1.1 wt% Pd/CeO_2 and the corresponding deconvolution indicating the contribution of Pd^0 with a binding energy of 334.44 eV (35.27 %) and Pd^{II} with a binding energy of 337.02 eV (64.72 %).
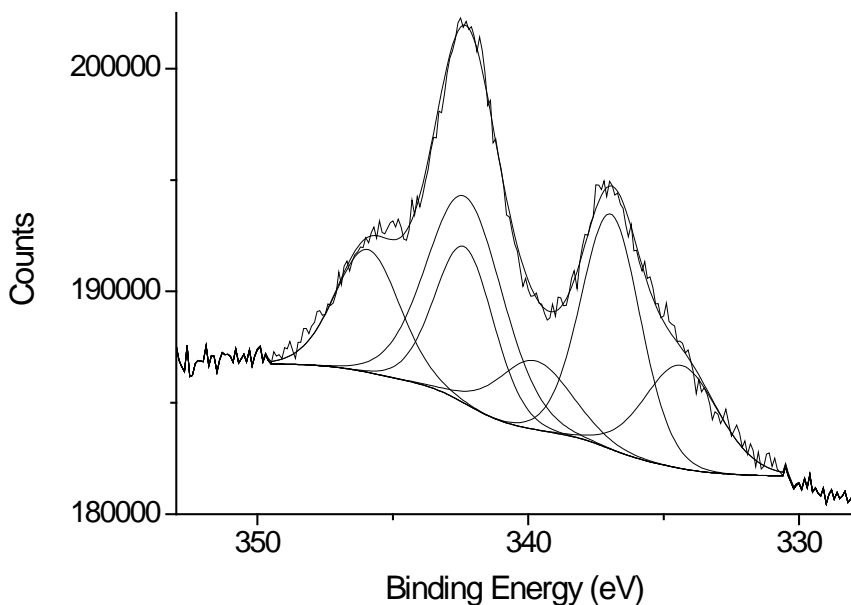
2.2. Hiyama coupling catalyzed by ligand-free supported metal catalysts.

To optimize the reaction conditions and to check the catalyst activity of the samples we selected the reaction of 4-iodotoluene (**1a**) with trimethylvinylsilane (**2a**) or triethoxyvinylsilane (**2b**) in DMF containing KF to give 4-methylstyrene (**3a**). Blank controls in the absence of metal-containing catalyst did not allow to detect any reaction product even for times much longer than those employed in the presence of palladium catalyst. Similarly, Pt/TiO_2 or Au/TiO_2 did not promote any reaction. In contrast to the previous unsuccessful experiments, all the palladium containing samples were able to catalyze the C-C coupling leading to the formation of 4-methylstyrene (**3a**) accompanied by lesser amounts of the expected trimethylsilyl derivatives **4a** and **5a** (see Table 1 and Scheme 1).

A summary of the results obtained for this ligand-free Hiyama coupling with vinylsilanes in the presence of the series of palladium catalysts is provided in Table 1. As it can be seen there, working at 130 ºC and at a Pd-substrate mol ratio of 1% very high conversions of aryl iodide were obtained using Pd NPs supported on MgO, C, CeO_2 and TiO_2. However, the selectivity towards the target 4-methylstyrene **3a** was only moderate due to the presence of significant amounts of the two stereoisomers **4a** as

well as the two stereoisomers of compound **5a**. Lower temperatures in the range of 60 to 100 ºC require longer reaction times to achieve similar conversions. However, even at lower temperatures the selectivity towards 4-methylstyrene **3a** did not improve, but in fact decreases significantly due to favoured formation of the stereoisomers **4a.** When triethoxyvinylsilane (**2b**) was used instead of trimethylvinylsilane (**2a**) as reagent and using Pd/TiO$_2$, Pd/MgO as heterogeneous or Pd(acac)$_2$ as homogenous ligand-free precatalysts, respectively (Table 1, entries; 10, 13 and 14), lower yields and selectivities to the target product (**3a**) were observed. These unsatisfactory results using triethoxyvinylsilane (**2b**) contrast with the common choice in the bibliography of alkoxysilanes derivatives as substrates due to their higher reactivity. Therefore it seems that trimethylvinylsilane (**2a**) is more appropriate reagent at this stage of this work. It happens that when using (**2b**) as reagent in the presence of Pd/MgO and Pd(acac)$_2$ almost complete conversion of 4-iodotoluene (**1a**) was attained but the product formed only accounts for a percentage of the substrate converted (Table 1, entries; 13 and 14), this should be probably due to the formation of non volatile products. We propose that hydrolysis of the ethoxy groups can lead to condensation and oligomerisation of silanes forming functionalized silicas that cannot be analysed by GC.

Table 1. Results of the ligand-free Hiyama cross-coupling of 4-iodotoluene (**1a**) and trimethylvinylsilane (**2a**) or triethoxyvinylsilane (**2b**) promoted by supported palladium nanoparticles or soluble palladium complexes. Reaction conditions: **1a**, 0.5 mmol; **2a** or **2b**, 0.6 mmol; KF, 1.2 mmol; DMF, 1.5 ml; Ar pressure, 2 bar; Metal/substrate ratio 1 mol%.
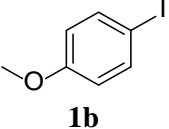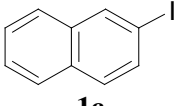

Entry	Catalyst	Substrate	T (ºC)	t (h)	Conv.[a] 1a (%)	Selec. 3a (%)	Yield 3a (%)
1	none	**2a**	130	24	0	-	-
2	Pt (5 wt%)/TiO$_2$	**2a**	130	23	0	-	-
3	Au (1.5 wt%)/TiO$_2$	**2a**	130	23	0	-	-
4	Pd (1.1 wt%)/CeO$_2$	**2a**	60	23	27	55	14[b]
5	Pd (1.1 wt%)/CeO$_2$	**2a**	100	22	99	62	60[c]
6	Pd (1.1 wt%)/CeO$_2$	**2a**	130	3	98	51	47[d]
7	Pd (3wt%)/C[e,f]	**2a**	130	24	45	90	38
8	Pd (3wt%)/C[e]	**2a**	130	9	98	72	70
9	Pd (1.09 wt%)/TiO$_2$	**2a**	130	3	97	76	73[g]
10	Pd (1.09 wt%)/TiO$_2$	**2b**	130	3	56	50	27[h]
11	Pd (1 wt%)/C	**2a**	130	8	84	74	60[i]
12	Pd (0.87 wt%)/MgO	**2a**	130	7	100	80	78
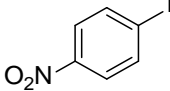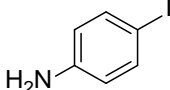
13	Pd (0.87 wt%)/MgO	**2b**	130	7	97	34	29[j]
14	Pd(acac)$_2$ (homogenous)	**2b**	130	7	99	41	39[j]

[a] Conversion based on **1a** disappearance. [b] The products observed include 13 % of (Z) and (E) **4a** isomers. [c] The products observed include 12 % of (Z) and (E) **4a** isomers. [d] The products observed include 15 % of (Z) and (E) **4a** isomers and 35 % of (Z) and (E) **5a** isomers. [e] Palladium/substrate ratio 2 mol%. [f] Without KF. [g] The product distrubution includes 15 % of (Z) and (E) **4a** isomers and 8 % of (Z) and (E) **5a** isomers. [h] The products observed include 5 % of (Z) and (E) **4a** isomers and 19 % of (Z) and (E) **5a** isomers. [i] The products observed include 16 % of (Z) and (E) **4a** isomers and 5 % of (Z) and (E) **5a** isomers. [j] No other products was detected by GC.

The scope of the Pd catalyst to promote cross coupling of aryl iodides with trimethylvinylsilane was studied by using a series of aryl iodides **1b-e**. The results of conversion, selectivity and yield towards the corresponding vinyl aromatics **3b-e** are listed in Table 2. As it can be seen in this Table, very high conversions are obtained using Pd NPs supported either on TiO$_2$, C or MgO. Interestingly the selectivity toward the vinyl aromatic (**3b-e**) was always significantly much higher than for compounds **4b-e**. Nevertheless, in the case of 4-iodoaniline (**1e**) the formation of the notable amount of the corresponding compound (**4e**) was observed (Table 2, entry; 6). Therefore, it appears that for this ligand-free Hiyama reaction the solid palladium catalysts can operate equally well even in the presence of strong electron donor substituent (methoxy group). There are precedents in the literature showing similar catalytic activity for methoxy substituted aryl iodide as the one observed here.[27]

Table 2. Results of Hiyama cross-coupling of aryl iodides with **2a** promoted by supported palladium catalysts. Reaction conditions: aryl iodide, 0.25 mmol; **2a**, 0.3 mmol; KF, 0.6 mmol; DMF, 1 ml; Ar pressure, 2 bar; Pd/substrate ratio 1 mol%.

Entry	Catalyst	Substrate	t (h)	Conv.[a] (%)	Selec. (%)	Yield (%)
1	Pd (1.1 wt%)/TiO$_2$	**1b**	1.5	99	85	83[b] (**3b**)
2	Pd (1.1 wt%)/TiO$_2$	**1c**	3	97	86	82 (**3c**)

3	Pd (0.87 wt%)/MgO	**1c**	6	99	92	90 (**3c**)
4	Pd (3wt%)/C[c]	![1d: O₂N-C₆H₄-I] **1d**	2	99	90	86 (**3d**)
5	Pd (0.87 wt%)/MgO	![1e: H₂N-C₆H₄-I] **1e**	9	99	76	73 (**3e**)
6	Pd (1wt%)/C	**1e**	10	98	65	61[d] (**3e**)

[a] Conversion based on aryl iodide disappearance 14 % of (Z) and (E) **4b**. [c] Pd/substrate ratio 2 mol%.[d] 30 % of (Z) and (E) **4e**.
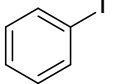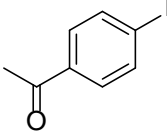
In order to check the influence of vinylsilane (**2a**) on the selectivity of the ligand-free Hiyama coupling with aryl iodide, we performed this reaction using symmetric tetravinylsilane **2c** instead of trimethylvinylsilane **2a** as reagent. The results using silane **2c** are summarized in Table 3. As it can be seen there, blank controls in the absence of any metal catalysts/ or using supported Pt or Au NPs lead to none or low conversions of **1a** at long reaction times. In contrast, all the palladium catalysts give almost complete conversion of **1a-g** even at much shorter reaction time. Interestingly, no vinylsilane byproduct **4a-g** was observed in any case. It was observed when using Pd/MgO or Pd/C as catalysts and **2c** as reagent that the overall selectivity towards the target styrene **3a-g** was higher than when using trimethylvinylsilane **2a** [see Fig. S7 in the Supporting Information for the temporal evolution of 2-iodonaphthalene (**1c**) as substrate and 2-vinylnaphthalene (**3c**) as final product using Pd (3 wt%)/C as the catalyst and also Table 3, entry 11]. Nevertheless it should be commented that for Pd/TiO$_2$ and Pd/CeO$_2$ very high selectivity towards the target substituted styrene **3a** was achieved at very high conversions. Therefore, **2c** as reagent gives better results than silane **2a**.

As it can see in Table 3 (entries, 13-16), when sufficient amount of KF is added, high conversions for times ranging from 5 to 12 h were achieved with excellent selectivity, giving very high yields of the desired 4-aminostyrene (**3e**). It is interesting to compare the yields of **3e** obtained using **2a** (Table 2, entries; 5 and 6) with those obtained using **2c** as reagent (Table 3, entries; 13 and 15). From the data presented for Pd/MgO and Pd/C it can be concluded that tetravinylsilane (**2c**) as reagent renders 4-aminostyrene (**3e**) with higher yield and in much shorter time than using silane **2a** as vinyl transfer reagent, thus confirming the advantages of using compound **2c**. This

could be due to the easier Si-C cleavage effected by F⁻ when vinyl groups are bonded to Si as in **2c** compared to when CH$_3$ are bonded to Si as in **2a**.

Table 3. Results for the Hiyama coupling of compounds **1a-g** with tetravinylsilane **2c** promoted by supported palladium catalysts. Reaction conditions: **1a-g**, 0.25 mmol; **2c**, 0.075 mmol; KF, 0.6 mmol; DMF, 1 ml; Ar, 2 bar; Pd/substrate ratio 1 mol%.


Entry	Catalyst	Substrate	t (h)	Conv.[a] (%)	Selec. (%)	Yield[b] (%)
1	Pt (1.37 wt%)/MgO	**1a**	23	7	-	-
2	Au(1.5 wt%)/TiO$_2$	**1a**	23	13	-	-
3	Pd (3 wt%)/C	**1a**	3	99	96	95[c]; **3a** (93)
4	Pd (1.09 wt%)/TiO$_2$	**1a**	6	97	92	89[c] (**3a**)
5	Pd (1.1 wt%)/CeO$_2$	**1a**	7	99	93	92[c] (**3a**)
6	Pd(OAc)$_2$ (homogenous)	**1a**	5	99	75	72 (**3a**)
7	Pd(acac)$_2$ (homogenous)	**1a**	5	99	95	94 (**3a**)
8	Pd(dba)$_2$ (homogenous)	**1a**	5	98	94	90 (**3a**)
9	Pd (3 wt%)/C	**1b**	5	99	92	91; **3b** (94)
10	Pd(acac)$_2$ (homogenous)	**1b**	3	99	95	93 (**3b**)
11	Pd (3 wt%)/C	**1c**	5	99	94	92; **3c** (95)[d]
12	Pd (3 wt%)/C	**1d**	4	100	91	88 (**3d**)
13	Pd (0.87 wt%)/MgO	**1e**	5	99	98	97 (**3e**)
14	Pd (3 wt%)/C[e]	**1e**	7	80	97	76 (**3e**)
15	Pd (3 wt%)/C	**1e**	7	99	97	95 (**3e**)
16	Pd (1.09 wt%)/TiO$_2$ (Fresh)	**1e**	9	99	97	96 (**3e**)
17	Pd (1.04 wt%)/TiO$_2$ (Second use)[f]	**1e**	10	99	93	91[g] (**3e**)
18	Pd (1.03 wt%)/TiO$_2$ (Third use)[f]	**1e**	12	99	95	93 (**3e**)

19	Pd (3 wt%)/C	1f	7	99	94	92[h]; **3f** (94)
20	Pd (3 wt%)/C	1g	5	99	78	75[i] (**3g**)

[a] Conversion based on **1a-g** disappearance. [b] Numbers in brackets correspond to yields determined independently by ^{1}H-NMR spectroscopy using acetonitrile or acetone as internal standards (entries 3, 9, 11 and 19). [c] the products observed include a small amount of **5a** isomers. [d] Reaction was carried out using: **1c**, 0.5 mmol; **2c**, 0.15 mmol; KF, 1.2 mmol; DMF, 1.5 ml; Ar, 2 bar; Pd/substrate ratio 1 mol%. [e] only 0.2 mmol of KF are used. [f] Pd (1.09 wt%)/TiO$_2$ catalyst recovered from the first reaction, washed with water (pH = 7), acetone, diethyl ether and dried. [g] The product observed include 6 % of (Z) and (E) **5e** isomers. [h] the products observed include a small amount of **5f** isomers. [i] The product observed include 18 % of (Z) and (E) **5g** isomer.

When aryl iodides with para substituents were reacted with tetravinylsilane (**2c**) in the presence of Pd (3 wt%)/C (see Table 3 entries; 3, 9, 12, 15, 19 and 20 and Scheme 1), the corresponding styrenes **3a-b** and **3d-g** were obtained with high conversion and high selectivity. A good linear relationship between Hammett σ^+ constant of the para substituent and the initial reaction rate (r_0) is observed [Figure 2 (a)]. Table 3 also summarizes the relative activity of supported palladium as heterogeneous catalysts compared to common phosphine-free palladium complexes acting as homogenous catalysts. The purpose is to put into context the catalytic activity of Pd (3 wt%)/C compared to conventional homogenous palladium catalysts Pd(acac)$_2$, Pd(dba)$_2$ and Pd(OAc)$_2$ for the ligand-free Hiyama reaction of compounds **1a** and **2c**. Under the same reaction conditions it was found that Pd (3 wt%)/C and Pd(acac)$_2$ are more active than Pd(dba)$_2$ and Pd(OAc)$_2$ [see Table 3 entries; 3 and 6-8 and Figure 2 (b)].

Figure 2. a: Plot of the initial reaction rate (r_0) vs. The σ^+ Hammett constant for the ligand-free Hiyama coupling of aryl iodides **1a-b** and **1d-g** with tetravinylsilane (**2c**) catalyzed by Pd (3 wt%)/C. b: Time-yield plots for reaction of 4-iodotoluene (**1a**) and tetravinylsilane (**2c**) to give 4-methylstyrene (**3a**) in the presence of: Pd (3 wt%)/C (■), Pd(acac)$_2$ (▲), Pd(dba)$_2$ (◆) and Pd(OAc)$_2$ (×) as catalysts respectively. Reaction conditions: **1a-b** and **1d-g**, 0.25 mmol; **2c**, 0.075 mmol; KF, 0.6 mmol; DMF, 1 ml; Ar pressure, 2 bar; Pd/substrate ratio 1 mol%.
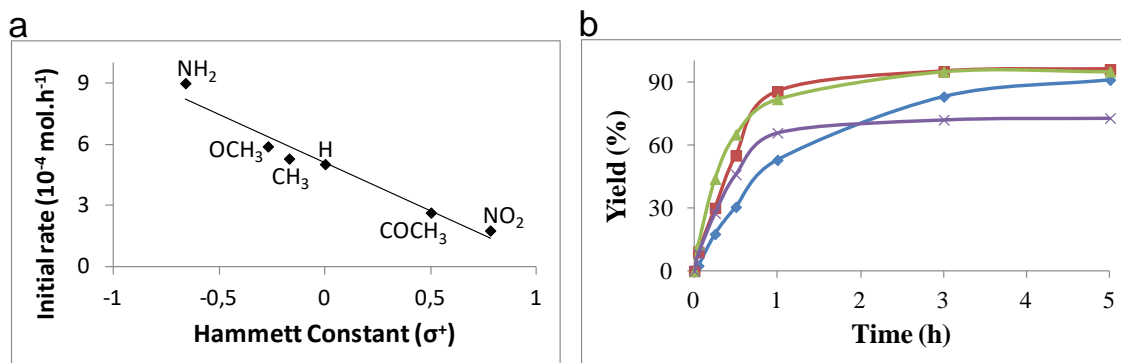
To assess the relative activity of our heterogeneous palladium catalysts, the reactivity of different aryl halides was checked. Particularly, considering the difficulty to obtain aryl iodides, it is important to test if aryl bromides can also be suitable substrates for the Hiyama free-ligand reaction with vinylsilanes. To evaluate this possibility we performed the reaction of 1-bromo-4-nitrobenzene (**1f**) with tetravinylsilane (**2c**) catalyzed by supported palladium NPs. The results are presented in Table 4. It was found that no coupling occurs in the absence of any catalyst even at very long reaction times. In contrast, very high yield with almost complete selectivity towards 4-nitrostyrene (**3f**) as achieved using either Pd/TiO$_2$ or Pd/MgO as catalyst. Thus, it was concluded that both Pd catalysts are similarly efficient to promote this Hiyama coupling, but it was observed that when an acid solid such as TiO$_2$ is used as support the reaction is complete in only 2 h (Table 4, entry 1) while 6 h are needed when a basic support is used such as MgO (Table 4, entry 2).

Table 4. Results of the Hiyama coupling of compound **1h** and **2c** promoted by supported Pd catalysts. Reaction conditions: **1h**, 0.25 mmol; **2c**, 0.075 mmol; KF, 0.6 mmol; DMF, 1 ml; Ar pressure, 2 bar; Pd/substrate ratio 1 mol%.


Entry	Catalyst	t (h)	Conv.[a] (%) 1h	Selec. (%) 3h	Yield (%) 3h
1	Pd (1.09 wt%)/TiO$_2$	2	99	98	95[b]
2	Pd (0.87 wt%)/MgO (Fresh)	6	98	97	94[b]
3	Pd (0.83 wt%)/MgO (Second use)[c]	9	99	92	91[d]
4	Pd (0.81 wt%)/MgO (third use)[c]	11	99	91	90[d]

[a] Conversions based on **1h** disappearance. [b] the product observed include a small percentage of (Z) **5h** isomer. [c] Pd (0.87 wt%)/MgO catalyst recovered, washed with

water (pH = 7), acetone, diethyl ether and dried. [d] The product distribution includes 7 % of (Z) **5h** isomer.

Figure 3 (a) presents the temporal evolution of aryl bromide **1h** and styrene **3h** (yield and selectivity) using Pd (1.1 wt%)/TiO$_2$ as catalyst (Table 4, entry 1), showing that the coupling proceeds with high efficiency. Hot filtration test [Figure 3 (b)] in which the solid catalyst is filtered after 15 min while the reaction mixture is still hot shows that the reaction between **1h** and **2c** stops in the absence of the solid catalyst.

Figure 3. a: Time-conversion plot for the reaction of 1-bromo-4-nitrobenzene (**1h**) and tetravinylsilane (**2c**) in the presence of Pd (1.1 wt%)/TiO$_2$. b: Hot filtration test for the reaction shown in part "a" upon filtration of the solid catalyst while hot after 0.25 h. (◆): disappearance of 1-bromo-4-nitrobezene (**1h**); (▲): yield of 1-nitro-4-vinylbenzene (**3h**); (■): selectivity of 1-nitro-4-vinylbenzene (**3h**).
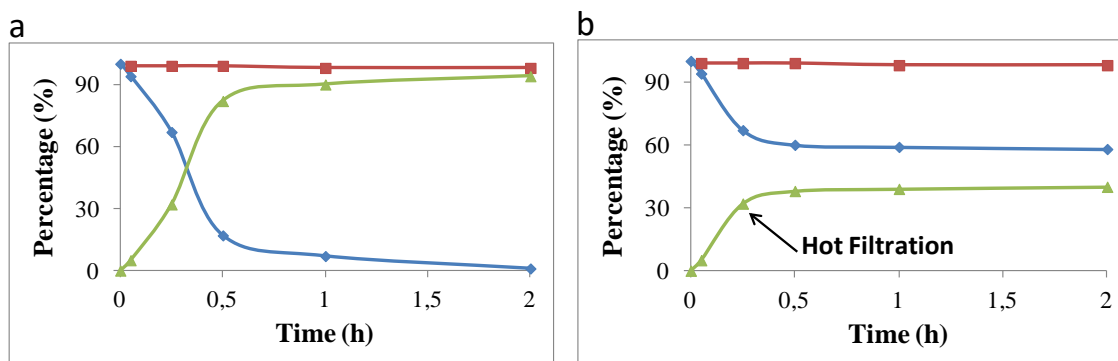
The double Hiyama coupling using silane **2c** as reagent, meta and para diiodobenzene (**1i** and **1j**) as substrate and supported palladium NPs as catalyst was also studied. The results are presented in Table 5; controls in the absence of any solid catalyst do not allow the detection of any product. In contrast, palladium catalyst promoted efficiently the double C-C coupling to the corresponding meta and para divinylbenzene **3i** and **3j**.


Table 5. Results of the double coupling of diiodobenzene (**1i**, meta or **1j**, para) by silane (**2c**) promoted by supported palladium catalysts. Reaction conditions: **1i** or **1j**, 0.25 mmol; **2c**, 0.15 mmol; KF, 1.2 mmol; DMF, 1 ml; Ar pressure, 2 bar; Pd/substrate ratio 1 mol%.

Catalyst / KF/130 °C
Ar(2 bar), DMF

1i, meta
1j, para

2c

3i, meta
3j, para

Entry	Catalyst	Substrate	t (h)	Conv. (%)	Selec. (%)	Yield (%)
1	Pd (1.09 wt%)/TiO$_2$	**1i**	1.5	99[a]	92	90[b]
2	Pd (1 wt%)/C	**1i**	2.5	100[a]	95	94[c]
3	Pd (0.87 wt%)/MgO	**1i**	3	100[a]	83	81[d]
4	Pd (1.09 wt%)/TiO$_2$	**1j**	1.5	99[e]	82	80[f]
5	Pd (0.87 wt%)/MgO	**1j**	3	100[e]	94	93[g]

[a] Conversion based on compound **1i**. [b] the products observed include 1 % of 1-iodo-3-vinylbenzene (**3i'**) and 5 % of (*E*)-1,2-bis(3-vinylphenyl)ethene (**5i**). [c] the products observed include 2 % of (*E*)-1,2-bis(3-vinylphenyl)ethene (**5i**). [d] the products observed include 6 % of 1-iodo-3-vinylbenzene (**3i'**) and 11 % of (*E*)-1,2-bis(3-vinylphenyl)ethene (**5i**). [e] based on compound **1j**. [f] the products observed include 11 % of 1-iodo-4-vinylbenzene (**3j'**) and 5 % (*E*)-1,2-bis(4-vinylphenyl)ethene (**5j**). [g] the products observed include 3 % of (*E*)-1,2-bis(4-vinylphenyl)ethene (**5j**).

Figure 4 (a) shows the temporal evolution of the products derived from the meta-diiodobenzene (**1i**) using Pd/TiO$_2$ as catalyst. As it can be seen in this Figure, the percentage of the iodostyrene **3i'** arising from the replacement of a single iodide is never high since this primary product appears as instable. In contrast, the formation of the divinylbenzene (**3i**) presents an induction period and the product appears as secondary but stable reaction product. The final selectivity towards the double substitution is significantly high. It is observed that when TiO$_2$ is used as support, the reaction is faster than that when using MgO [see Figure 4 (b)]. Probably this is a reflection of the acid/base nature of the support influencing the performance of heterogeneous catalyst. Although in the case of Pd/MgO the intermediate compound **3j'** is also a primary and unstable, the accumulated percentage of **3j'** is higher than for Pd/TiO$_2$.

Figure 4. a: Time-conversion plot for reaction of 1,3-diiodobenzene (**1i**) and tetravinylsilane (**2c**) in the presence of Pd (1.1 wt%)/TiO$_2$. (◆): disappearance of 1,3-diiodobenzene (**1i**); (▲): yield of 1,3-divinylbenzene (**3i**); (■): selectivity of 1,3-divinylbenzene (**3i**); (×): yield of 1-iodo-3-vinylbenzene (**3i'**). b: Time-conversion plot for reaction of 1,4-diiodobenzene (**1j**) and tetravinylsilane (**2c**) in the presence of Pd (0.87 wt%)/MgO. (◆): disappearance of 1,4-diiodobenzene (**1j**); (▲): yield of 1,4-divinylbenzene (**3j**); (■): selectivity of 1,4-divinylbenzene (**3j**); (×): yield of 1-iodo-4-vinylbenzene (**3j'**).
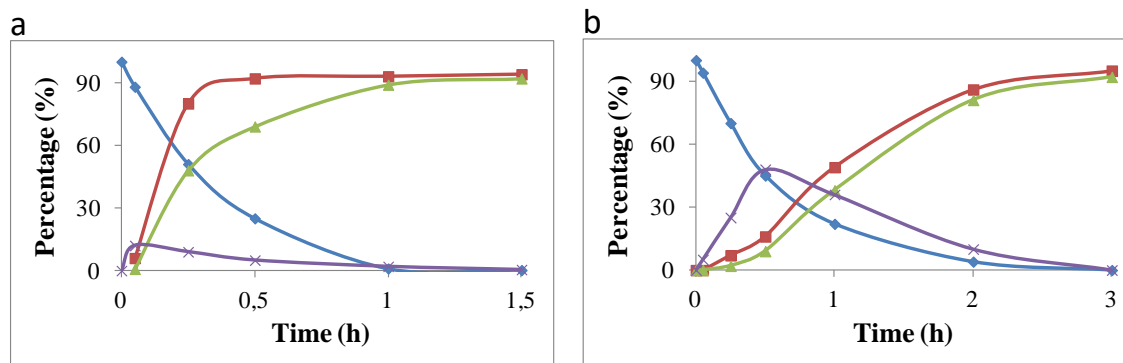
3. LEACHING AND REUSABILITY.

One important issue in heterogeneous catalysis using Pd NPs is to provide data in support of the heterogeneity of the process, addressing the possible contribution of Pd species leached from the solid to the liquid phase. To gain understanding on the possible contribution of leaching to the Hiyama coupling reaction, we performed the reaction of 4-iodoaniline (**1e**) and **2c** using Pd/TiO$_2$ as solid catalyst (see Table 3, entries 16-18) and also the reaction of 1-bromo-4-nitrobenzene (**1h**) and **2c** using Pd/MgO as solid catalyst (see Table 4, entries 2-4), and analyzed the Pd content of the solid catalysts at final reaction time. ICP analysis established that the palladium content was to 1.03 wt% (third use) and 1.04 wt% (second use) compared to the 1.09 wt% of Pd present in the starting frech Pd/TiO$_2$ catalyst. Similarly, in the case of Pd/MgO we also determine some depletion of Pd in the solid catalyst of 0.81 wt% (third use) and 0.83 wt% (second use) compared to 0.87 wt% of Pd present in the starting Pd/MgO catalyst.

In addition, we also studied the heterogeneity of the process performing the conventional hot filtration test in which after starting the reaction under normal conditions (Figure 3 a), the suspension is filtered at the reaction temperature after reacting an intermediate conversion and the clear solution in the absence of solid (Pd/TiO$_2$) is allowed to react further. In the present case, we have observed that after removal of the Pd/TiO$_2$ catalyst at 0.25 h, the reaction mixture in the absence of solid undergoes only limited conversion (< 7 %, see Figure 3 b) indicating that the contribution of leached Pd observed is not significant. In the literature there are precedents showing that related supported palladium catalysts undergo leaching when using DMF as solvent.[28] However, these precedents also show that the activity of the leached palladium species as catalyst depends on the substrates involved and how

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demanding is the catalytic reaction.[19, 28] In our case, it seems that the 0.05 wt% percentage of leached palladium with respect to 1.09 wt% of the starting Pd/TiO_2 catalyst is not very efficient to promote C-C coupling and that a large percentage of the products observed in the coupling reaction derive from the presence of the solid catalyst.

The hot filtration test has been frequently questioned, since unavoidable temperature decrease during filtration can cause deposition of the leached palladium on the solid. For this reason to further demonstrate catalyst heterogeneity of our Hiyama coupling of aryl halides and vinylsilanes producing styrene derivatives with supported Pd particle precatalysts, we performed the "*scavenging*" test by silica-bound thiol that is supposed to trap partially the soluble palladium species. Scavenging of soluble Pd species by silica-bond thiols has been proposed as a safe method for distinguishing between homogenous and heterogeneous catalysts. Figure 5 compares the time-yield plots of Pd (3 wt%)/C with different amounts of $SH(CH_2)_3$-SiO_2 for the reactions of 4-iodotoluene (**1a**) or 1-iodo-4-methoxybenzene (**1b**) with tetravinylsilane (**2c**) in DMF at 130 ºC containing KF to give 4-methylstyrene (**3a**) or 1-methoxy-4-vinylbenzene (**3b**), respectively. Figure 5 a and b present the temporal evolution of final yields of compounds **3a** and **3b** using various percentages of $SH(CH_2)_3$-SiO_2 as soluble Pd scavengers. For both substrates, it was found that the catalytic activity decreases by increasing the amount of solid scavenger in the reaction. This observation suggests that the true active Pd species are released from the solid to the solution and redeposit on the support upon cooling during the hot filtration test. This interpretation of the influence of solid scavengers also agrees with analytical data showing for three independent experiments the presence of 0.0085, 0.0052 and 0.0322 % Pd (with respect to the initial Pd amount) in the liquid phase for the coupling of 4-iodotoluene (**1a**) with tetravinylsilane (**2c**) in DMF at 130 ºC containing KF and Pd (1.09 wt%)/TiO_2 (Pd/substrate ratio 1 mol%) as solid catalyst monitored at 1, 2 and 4 h reaction time respectively. It should be, however commented that, recently, the scaveringing test in the presence of bases at temperatures in the range of 90-135 ºC has been questioned by Huang and co-workers[29], who have found that silica bound thiol can leach from the solid silica to the solution, due to dissociation of thiol groups from the silica, leading to poisoning and deactivation of solid Pd catalyst even if these solids did not leach any palladium species to the solution. In our case, blank controls boiling at 130 ºC silica-

bound propyl thiol in the presence of KF for a long period of time has allowed to detect the presence in the gas phase of a minimal quantity of propylthiol. This amount is, however, too small to justify the influence of silica-bond thiol on the activity of the solid catalyst.

Figure 5. Plots for the Hiyama coupling of aryl iodides **1a-b** with tetravinylsilane (**2c**) catalyzed by Pd (3 wt%)/C. a: Time-yields plots for reaction of 4-iodotoluene (**1a**) to give 4-methylstyrene (**3a**) in the presence of different molar percentages of SH/substrate (**1a**) ratio 0 (■), 2 (▲), 4 (×) and 8 mol % (◆) respectively. b: Time-yield plots for reaction of 1-iodo-4-methoxybenzene (**1b**) to give 1-methoxy-4-vinylbenzene (**3b**) in the presence of the following molar percentages of SH/substrate (**1b**) ratio 0 (■), 10 (▲) and 20 mol % (◆), respectively. Reaction conditions: **1a** or **1b**, 0.25 mmol; **2c**, 0.075 mmol; KF, 0.6 mmol; DMF, 1 ml; Ar pressure, 2 bar; Pd/substrate ratio 1 mol%.
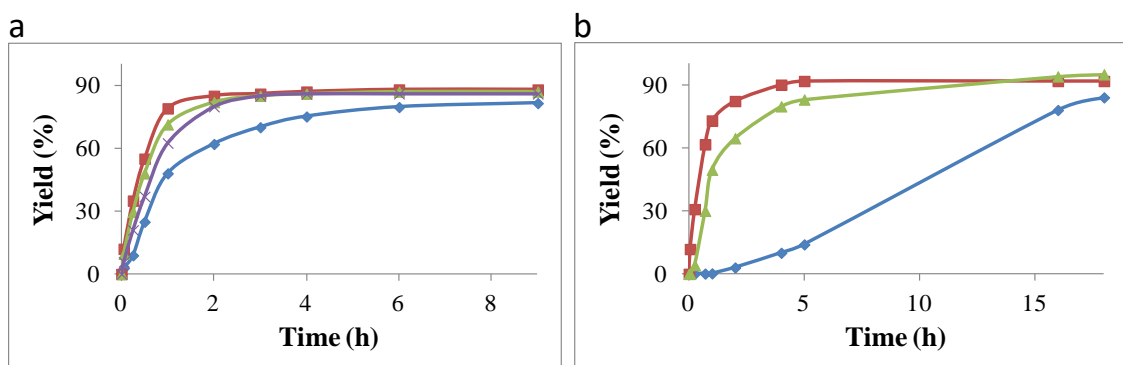

Regardless the occurrence or not of Pd leaching, another important point of a heterogeneous catalyst is its reusability for consecutive runs. This point was studied by recovering the catalyst at the end of the reaction, washing it and reuse for subsequent runs Table 3, entries; 16-18 and Table 4, entries; 2-4. The degree of deactivation was determined by comparing the time-conversion plots for the fresh and reused catalysts. It was observed that the catalyst undergoes a gradual decrease in the catalytic activity. To achieve the same yield of **3e** and **3h** larger reaction times were needed (see Tables 3 and 4). This gradual deactivation can be understood by the generation of I^- and Si-containing products during the reaction and the presence of KF that will deposit on to the catalyst. Also, the small percentage of Pd leaching or a possible Pd particle growth[30-32] [see TEM images of reused catalysts in the Supporting Information (Fig. S8 and Fig. S9)] could contribute to the decay of the catalyst activity as it has been observed in other cases.[32]

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4. REACTION MECHANISMS

The most likely reaction mechanism for the C-C coupling reaction based on the literature[33] and the available data is shown in Scheme 2. It involves the oxidative addition of Pd(0) to the C-X (I or Br) bond of arenes, subsequent nucleophilic attack (transmetallation) of vinyl anion and a final reductive elimination. Vinyl anions will be formed by cleavage of the C-Si bond by F$^-$ anions.[34]

Scheme 2. Proposed mechanism for the ligand-free Hiyama C-C coupling of vinylsilanes and arylhalides in the presence of heterogeneous palladium catalyst.
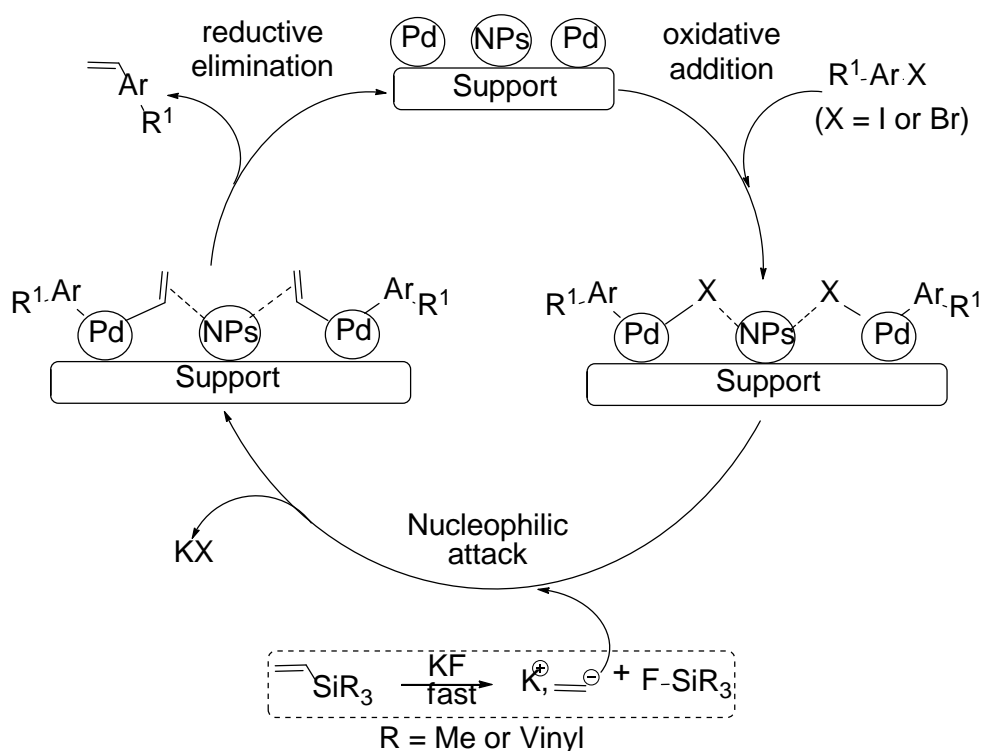
5. CONCLUSIONS

Herein we have developed a heterogeneous Hiyama C-C coupling reaction in which styrenes can be obtained with high yield and selectivity using reusable supported palladium NPs as heterogeneous catalysts in the absence of phosphine ligands. The key

point is the nature of the solid in which the Pd NPs are supported, MgO and TiO$_2$ being the most suitable supports tested. Pt and Au are inefficient to promote this reaction. Leaching tests suggest that there is some contribution of dissolved Pd since Pd in solution has been detected and the scavenging test decreases the initial reaction rate. However, hydrolysis of propylthiol under the reaction conditions takes place in some extent. Although the solid Pd catalyst can be reused, it was, however, observed that the palladium catalysts undergo a certain deactivation upon use that can be attributed to several factors including the presence of inorganic compounds on the catalyst, Pd leaching or agglomeration of Pd NPs.

6. EXPERIMENTAL SECTION

All reactions were carried out under Ar atmosphere. Solvent are high purity grade and used without further purification. Gas chromatography (GC) was performed with a Varian apparatus equipped with a flame detector (FID). The products were separated with a HP-5 capillary column (5% phenyl, 95% polymethylsiloxane, 30 m, 0.25 mm $\times$ 0.25 µm, Teknokroma) and identified by GC-MS, using a Fisons GC 8000 gas chromatograph equipped with a DB5 capillary column with a mass spectrometer detector (Fisons MD 800 quadrupole detector) (see Supporting Information). The identification of the products was also carried out by NMR spectroscopy; NMR spectra were obtained with a Bruker Avance 300 spectrometer working at 300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C. The ^{1}H spectra of the styrenes products were referenced to CDHCl$_2$ = 5.27 ppm or [D$_7$]DMF = 2.62, 2.80 and 7.92 ppm and the ^{13}C were referenced to CDHCl$_2$ = 53.84 ppm (see Supporting Information).

6.1. Catalyst preparation.

Pd/TiO$_2$, Pd/CeO$_2$ and Pd/MgO were obtained by impregnation of 2 g of commercial TiO$_2$, CeO$_2$ and MgO, respectively (calcined at 400 ºC for 4 h) with a mixture of deionized water (15 ml) and acetone (8 ml) solution of 35 mg of PdCl$_2$ (Aldrich, *purum*, 60 % palladium content). The slurry was stirred 15 h at room temperature, then all the liquid was evaporated and the solid was dried under vacuum at 100 ºC for 2 h and reduced with 1-phenyletanol at 160 ºC for 3 h. The catalyst was then filtered, washed (acetone and diethyl eter), and dried under vacuum at 100 ºC for 12 h.

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The final Pd content was found to be respectively 1.09, 1.10 and 0.87 wt% by atomic absorption analysis.

Pt(1.37 wt %)/MgO and Pt(5 wt %)/TiO$_2$ samples correspond to the catalysts previously reported by us.[35, 36]

The Pd/C catalysts containing of 1 and 3 wt % palladium on C were supplied by the Sigma-Aldrich Company.

The Au/TiO$_2$ catalyst containing of 1.5 wt % gold on TiO$_2$ was supplied by the World Gold Council (reference catalysts, Type A).

6.2 .Synthesis of styrene derivatives.

6.2.1. Preparation of styrene derivatives (3a-h):

A mixture of organohalides (**1a-h**) (0.25 mmol), vinysilanes **2a** (0.3 mmol) or **2c** (0.075 mmol), potassium fluoride (0.6 mmol) and supported palladium NPs catalyst (Pd/substrate ratio 1 mol%) was suspended in DMF (1 ml). Then the flask was evacuated under vacuum and refilled with argon. The evacuation/refilling cycle was repeated three times (pressure 2 bar). The mixture was stirred at 130 ºC and the reaction was monitored by GC and GC-MS. The reaction was performed for the time required ranging from 1.5 to 24 h, to obtain the maximum yield of **3a-h** products.

Spectral GC-MS *m/z* data for compounds **3a-h** (see the supporting information for details Figs. S10, S12, S14, S17-S19, S21)

Spectral NMR data for compounds **3a**, **3b**, **3c** and **3f** (see the supporting information for details Figs. S11, S13, S15-S16 and S20)

6.2.2. Preparation of divinylbenzene (3i-j):

A mixture of diiodobenzene (**1i-j**) (0.25 mmol), vinysilane **2c** (0.15 mmol), potassium fluoride (1.2 mmol) and supported palladium NPs catalyst (Pd/substrate ratio 1 mol %) was suspended en DMF (1 ml). Then the flask was evacuated under vacuum and refilled with argon. The evacuation/refilling cycle was repeated three times (pressure 2 bar). The reaction mixture was stirred at 130 ºC and the reaction was monitored by GC and GC-MS, for 3 h. During this time all of initials compounds **3i'-j'** formed arising from the replacement of a single iodide are reacted to obtain the maximum yield of products **3i-j.**

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Spectral GC-MS *m/z* data for compounds **3i**, **3i'**, **3j** and **3j'** (see the supporting information for details Figs. S22-S25)

Acknowledgements

Appendix A. Supplementary material

Supplementary data associated with this article (Experimental details and characterization data including XPS, TEM, liquid ^{1}H and ^{13}C NMR spectra and GC-MS of reaction products) can be found, in the online version, at http://

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