

Organically modified Pd–silica catalysts applied in Heck coupling

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Pd–silica catalysts prepared by depositing Pd onto silica precursors modified by surface methyl or phenyl groups through the reduction of Pd²⁺ ions with surface Si–H functions exhibit high activity and selectivity in Heck coupling.

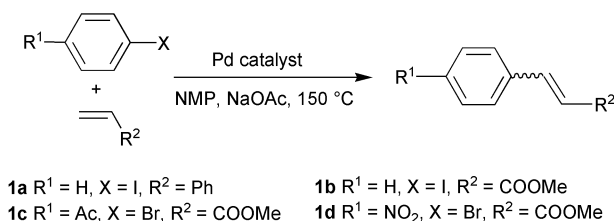
Coupling reactions to form carbon–carbon bonds are important transformations in organic synthesis. One of these, Heck coupling, allows the olefination of aryl, vinyl, benzyl, allyl halides, acetates or triflates through their reaction with various alkenes in the presence of palladium in a single step.¹ Most studies focused on the use of soluble Pd complexes with phosphine ligands.^{2,3} It was also shown, however, that heterogeneous Pd catalyst systems, namely stabilised colloidal palladium^{3–6} and supported palladium catalysts,^{7–12} are also active in the reaction. Most recent findings show that even Heck coupling of chloroarenes can be induced by heterogeneous Pd catalysts to give the corresponding vinylarenes in high yields under appropriate reaction conditions.^{11,13}

For economic reasons development of heterogeneous, that is reusable, catalysts for industrial applications remains an important goal. This is a particular challenge for Heck coupling since leaching of Pd from heterogeneous catalyst systems is known to occur under certain reaction conditions.^{7,8,10,14} The main goal of the present study, therefore, is the preparation, characterisation, and evaluation in Heck coupling of new, organically modified heterogeneous Pd–silica catalysts.

A novel method for the controlled deposition of metals onto surfaces was disclosed by Fry in the early 1990's.^{15,16} It was shown that the treatment of silica with trichlorosilane allows the immobilisation of the Si–H function. This surface hydrosilane function is capable of reducing metal ions resulting in the deposition of a thin metal layer onto the silica surface.

We have prepared two series of catalysts by modifying the original synthesis protocol. First, we treated silica (Aldrich, Davisil grade 363, dried at 500 °C for 2 h) with various chlorohydrosilanes (trichlorosilane, dichloromethyl- and chlorodimethyl-silane, dichlorophenyl- and chlorodiphenyl-silane) to prepare organically modified silica materials. The modified silicas were reacted with a saturated solution of PdCl₂ in methanol (1 g silica, 71 mg PdCl₂ in 160 ml methanol) to get five Pd-on-silica catalysts with various Pd loadings.

The catalysts were found to exhibit high activity in the Heck coupling of iodobenzene with styrene (**1a**) or methyl acrylate (**1b**) (Scheme 1) using equal amounts of catalyst to yield the corresponding *E* isomers with good or excellent selectivities (Table 1)† as evidenced by GC, GC-MS and liquid NMR of the isolated products.



Scheme 1 Heck coupling.

For a better comparison of the catalytic performance of these new catalyst materials, a second set of catalysts was prepared by reacting 1.994 g of the modified silica samples with a 1.25 × 10^{−3} M PdCl₂ solution (10 mg PdCl₂ in 45 ml methanol) to get five catalysts with equal Pd loading of 0.3 wt%. The resulting silica precursors and the samples loaded with Pd were characterised by physical methods (Table 2). Reaction with silanes results in some decrease in the BET surface area of the parent silica (455 m² g^{−1}), whereas deposition of Pd has the opposite effect in most cases. According to TEM characterisation the samples have a narrow range of particle sizes and are of low dispersion.

The silica precursors analysed by ²⁹Si CP-MAS NMR spectroscopy showed two major resonances at about −102 ppm (Q³) and −111 ppm (Q⁴) characteristic of SiO₄ units possessing 3 and 4 siloxane bridges, respectively. When organic functionalities (methyl or phenyl groups) were introduced to the surface new signals with higher chemical shifts appeared originating from the polarization transfer of methyl and phenyl protons (Table 2). ¹³C CP-MAS NMR spectroscopy showed resonances at −2.1 ppm (methyl groups) and 127.1, 129.7 and 132.5 ppm (phenyl groups). The spectra also show a signal at 48.3 ppm, which is due to methoxy groups attached to silicon. These are formed when in the final step of the preparation of the silica precursors, samples are treated with methanol to transform unreacted Si–Cl functions.

The 0.3% Pd–silica catalysts exhibit lower activity in the coupling of iodobenzene with styrene (**1a**) because of the lower amount of Pd present in the reaction mixture (0.3 mol% with respect to iodobenzene) but the reaction takes place with increased selectivities (Table 3).‡ It is significant that even less

Table 1 Catalytic performance of Pd–silica catalysts with various Pd loading in Heck coupling

Catalyst	Pd content (wt%)	1a		1b	
		Conv. (%)	Sel. (%)	Conv. (%)	Sel. (%)
Pd/SiO ₂	1.47	100	90	65	100
Pd/SiO ₂ Me	0.97	93	84	59	100
Pd/SiO ₂ Me ₂	1.28	75	84	85	100
Pd/SiO ₂ Ph	1.12	100	80	85	100
Pd/SiO ₂ Ph ₂	0.35	65	85	75	100

Table 2 Characterisation of silica precursors and Pd–silica catalysts

Silica precursors			0.3% Pd–silica catalysts		
Silane ^a	BET/m ² g ^{−1}	²⁹ Si NMR (ppm)	Catalyst	BET/m ² g ^{−1}	Particle size ^b /nm
Cl ₃ SiH	390		Pd/SiO ₂	419	9–11
Cl ₂ MeSiH	416	−35.5	Pd/SiO ₂ Me	430	12–15
ClMe ₂ SiH	398	−2.2	Pd/SiO ₂ Me ₂	451	21–24
Cl ₂ PhSiH	417	−47.1	Pd/SiO ₂ Ph	371	12–15
PhPh ₂ SiH	379	−18.7	Pd/SiO ₂ Ph ₂	430	9–13

^a Silanes used in treatment of silica. ^b Pd particle sizes, determined from TEM as the average diameter of about 100 particles.

Table 3 Catalytic performance of 0.3% Pd–silica catalysts in Heck coupling

Catalyst	1a	1b	1c	1d
Pd/SiO ₂	54 ^a (86) ^b	81 ^a (99) ^b	47 ^a (99) ^b	64 ^a (99) ^b
Pd/SiO ₂ Me	58 (86)	84 (99)	67 (99)	100 (99)
Pd/SiO ₂ Me ₂	35 (85)	54 (99)	19 (99)	68 (99)
Pd/SiO ₂ Ph ^c	80 (83)	97 (99)	75 (99)	100 (99)
Pd/SiO ₂ Ph ₂	57 (86)	51 (99)	58 (99)	66 (99)

^a Conversion (%), ^b Selectivity (%), ^c Turnover frequencies for this catalyst vary between 2 min^{−1} and 72 min^{−1} for the four reactions (Pd dispersion measured by hydrogen chemisorption is 0.04).

reactive activated bromoarenes (*p*-bromoacetophenone **1c** and *p*-bromonitrobenzene **1d**) react satisfactorily with styrene.

It is seen from these data that the organophilicity of the surface has a strong effect on catalytic performance. Namely, catalysts prepared from precursors with a single organic group as surface modifier (Pd/SiO₂Me and Pd/SiO₂Ph) show increased activity whereas activities decrease with the introduction of two methyl or phenyl groups (Pd/SiO₂Me₂ and Pd/SiO₂Ph₂). This effect is more pronounced in the reaction of the less reactive bromoarenes (Table 3, **1c** and **1d**).

The heterogeneity of the catalyst samples was also evaluated. As mentioned significant amounts of Pd were shown to leach out from heterogeneous Pd catalysts and the reaction may be mainly catalysed by Pd species in the liquid phase.^{8,9} It is also known that almost all Pd is redeposited after completion of the reaction. Therefore, as pointed out by Arai,⁸ a true evaluation of heterogeneity can be done by interrupting the reaction at low conversion and then continuing the process with both the catalyst and the filtrate. In this way, information about the presence or absence of active species in solution and the activity of such species can be acquired.

Tests were carried out accordingly by reacting iodobenzene with styrene using 0.3% Pd/SiO₂Ph, which proved to be the best catalyst. Conversion values thus determined are presented in Table 4. Under standard conditions (entries 1–3) there is a small increase in conversion in the filtrate after catalyst removal in the first 15 min, and then there are no further changes. Similar observations can be made when toluene is used as solvent instead of NMP and with triethylamine as base (entries 4–6). The amount of Pd present in the solution determined by ICP is about 1 ppm in this latter case, that is, less than 1% of the Pd is dissolved from the silica support. These observations indicate that only a very small fraction of Pd dissolved and this amount of metal in solution does not appear to be active as a homogeneous catalyst in the transformation.

Finally, catalyst recycling studies were performed using 0.3% Pd/SiO₂Ph and a 10% Pd-on-C catalyst (Aldrich) for comparison. Results given in Table 5 show that catalyst performance practically does not change in successive experi-

Table 4 Leaching tests with a 0.3% Pd/SiO₂Ph catalyst in Heck coupling of iodobenzene and styrene

Entry	Conv. (%) [split time/min]	Conv. (%) [time/min]		Pd in solution (ppm) ^c
		Suspension	Filtrate	
1 ^a	53 [15]	69 [15]	64 [15]	2.8
2 ^a		84 [45]	64 [45]	2.1
3 ^a		90 [75]	60 [75]	2.8
	Conv. (%) [split time/h]	Conv. (%) [time/h]		
		Suspension	Filtrate	
		Suspension	Filtrate	
		Suspension	Filtrate	
4 ^b	40 [6]	57 [6]	46 [6]	0.7
5 ^b		67 [12]	45 [12]	1.45
6 ^b		73 [18]	49 [18]	1.7

^a Standard reaction with 68 mg of catalyst. ^b Reaction in toluene with 68 mg of catalyst and triethylamine as base. ^c Determined by ICP.

Table 5 Catalyst recycling in Heck coupling of iodobenzene and styrene

Reaction	Catalyst treatment ^a	0.3% Pd/SiO ₂ Ph		10% Pd/C	
		Conv. (%)	Sel. (%)	Conv. (%)	Sel. (%)
1		94	85	100	84
2	A	96	84	96	84
3	A	94	83	97	84
1		98	85	97	85
2	T	92	86	99	86
3	T	99	86	94	84

^a A: washed with acetone, water and acetone and air-dried (1 h). T: washed with toluene and dried *in vacuo* (12 h).

ments. These results indicate that properties of our new organically modified catalysts are identical with those of 10% Pd/C, the best commercial catalyst for heterogeneous Heck coupling.

In summary, we have demonstrated the feasibility of a novel approach for the synthesis of organically modified Pd–silica catalysts and showed that this new catalyst family has great potential in Heck coupling under heterogeneous conditions. A strong effect of the organophilicity of the surface on catalytic performance was also found.

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Notes and references

† General reaction conditions: Equimolar amounts (0.89 mmol) of aromatic halide, alkene, and NaOAc, 27.3 mg catalyst, 2 ml *N*-methyl-2-pyrrolidone (NMP) and decane or biphenyl (internal standards) were stirred in a sealed tube at 150 (± 1) °C for 5 h (styrene) or 2 h (methyl acrylate). No special precaution was taken to exclude air or moisture. Conversion and selectivity were determined by GC analysis.

‡ 68 mg of the 0.3% Pd–silica catalysts was used in these studies.

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