

Polysilane-supported Pd and Pt nanoparticles as efficient catalysts for organic synthesis†

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Polysilane-supported Pd and Pt catalysts have been prepared for the first time, and used successfully in hydrogenation, Suzuki and Sonogashira reactions, and hydrosilylation respectively: the reactions proceeded in high yields, and the catalysts could be recovered almost quantitatively by simple filtration and reused.

Transition metal complexes have played important roles as catalysts for various transformations in organic synthesis.¹ While homogeneous transition metal catalysts are often used due to their high activity and availability, they are expensive, air-sensitive, and in many cases cannot be recovered and reused. To address these issues, the immobilization of homogeneous catalysts onto inorganic or organic supports has been widely investigated.² However, tedious procedures are often needed for the preparation of such heterogeneous catalysts, and the lower activity/selectivity and the leaching of catalysts from the supports are serious problems. In the course of our investigations to develop efficient heterogeneous catalysts, we focused on polysilane as a support of heterogeneous catalysts. Polysilane has been widely studied due to its interesting electronic properties, such as high hole mobility, photoconductivity, and nonlinear optical properties caused by σ -conjugation of the silicon backbone.^{3–5} In addition, polysilane is used as a starting material for ceramics, and synthetic methods for mass production are established.⁶ However, to the best of our knowledge, there are no reports on the use of polysilane as a support of heterogeneous catalysts.^{7,8} In this paper, we describe the first example of highly active, recoverable and reusable polysilane-supported Pd and Pt catalysts, their preparation and application to hydrogenation, Suzuki and Sonogashira reactions, and hydrosilylation.

Recently, we have developed new methods for immobilizing metal catalysts onto polymers, microencapsulation,⁹ and polymer incarcerated methods,¹⁰ which are based on the physical envelopment by the polymers, and on the electronic interaction between the π electrons of the benzene rings of polystyrene-based polymers and the vacant orbitals of metals. We first examined several reaction conditions for the preparation of polysilane-supported palladium catalysts (PSi–Pd) using the microencapsulation technique (Table 1). Poly(methylphenylsilane) (**1**, $M_w = 3.2 \times 10^4$) and several Pd(II) salts were chosen as the polysilane and Pd(II) sources, respectively. When the Pd(II) salts were reduced using NaBH₄ or

Table 1 Preparation of PSi–Pd **2a–e**

Entry	Pd Source	Reductant	Temp/°C, Time/h	PSi–Pd Loading ^a / mmol g ⁻¹	Yield of Pd (%)
1	Pd(PPh ₃) ₄	none	rt, 2	2a 0.131	93
2	Pd(OAc) ₂	none	0, 1; rt, 1	2b 0.134	96
3	Pd(OAc) ₂	NaBH ₄ (5 eq.)	0, 1; rt, 1	2c 0.121	90
4	Pd(NO ₃) ₂	NaBH ₄ (5 eq.)	rt, 4	2d 0.0947	83
5	PdCl ₂	H ₂ (1 atm)	rt, 4	2e 0.0934	79
6	Pd(NO ₃) ₂	H ₂ (1 atm)	rt, 4	2f 0.106	94

^a Determined by ICP analysis.

H₂, PSi–Pd **2c–e** with Pd loadings of 0.0934–0.121 mmol g⁻¹ were prepared. Interestingly, Pd(PPh₃)₄ and Pd(OAc)₂ were immobilized without any reductants to form PSi–Pd **2a** and **2b** with higher Pd loadings.

We then evaluated PSi–Pd **2a–e** in the hydrogenation of ethyl cinnamate using 0.5 mol% Pd (Fig. 1). In the case of using **2a**, **2b**, or **2c**, the reaction was completed within 60 min, while the reaction using **2d** or **2e** was slower. PSi–Pd **2f** showed much less activity.†

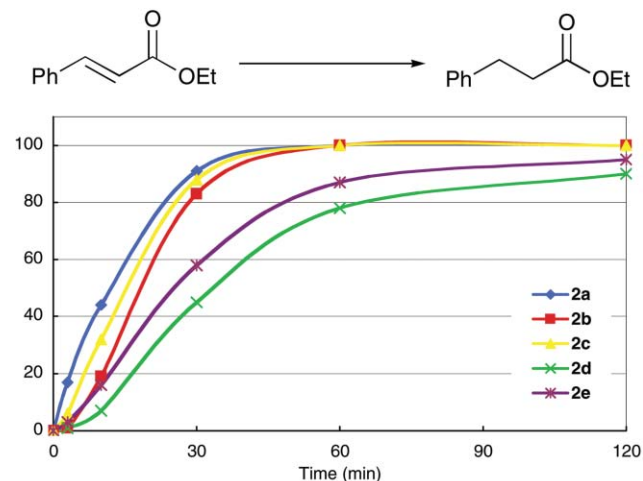


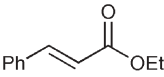
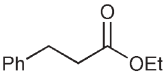
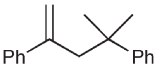
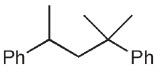
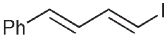
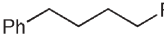
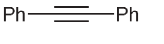
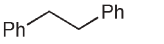
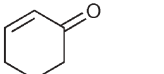
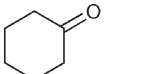
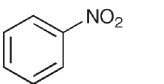
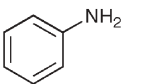
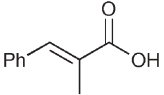
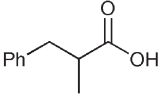
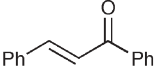
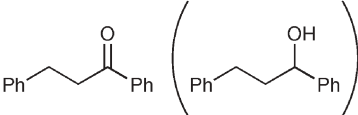
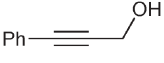
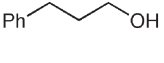


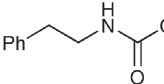

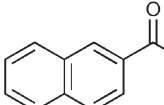
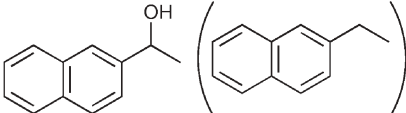
Fig. 1 Hydrogenation of ethyl cinnamate in the presence of 0.5 mol% of PSi–Pd **2a–e**. Reaction conditions: ethyl cinnamate (1 mmol), PSi–Pd (0.5 mol%), hexane (3 mL), and H₂ (1 atm) at room temperature. The conversions were determined by GC analysis.

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† Electronic supplementary information (ESI) available: Experimental and TEM images of **2a**, **2b**, and **2f**. See DOI: 10.1039/b610241g

Table 2 PSi–Pd **2b**-Catalyzed hydrogenation

Entry	Substrate	Time/h	PSi–Pd 2b (0.5 mol%) Substrate $\xrightarrow[1.0 \text{ mmol}]{\text{H}_2 \text{ bubbling, hexane (3 mL), rt}}$ Product		Yield (%) ^a	Leaching (%) ^c
			Product			
1		1			>99 ^b	<0.08
2		2			97	<0.08
3		2			>99	<0.08
4		3			>99	<0.08
5		2			>99 ^b	<0.08
6		1.5			>99 ^b	2.28
7 ^d		6			97	<0.08
8 ^d		9			84(13)	<0.08
9 ^d		2			96	<0.08
10 ^d		10			>99	0.40
11 ^d		10			93	5.41
12 ^d		36			86(9)	0.13

^a Determined by ¹H NMR analysis with reference to an internal standard (IS = durene). ^b Determined by GC analysis. ^c Determined by ICP analysis. ^d Ethanol was used as a solvent.

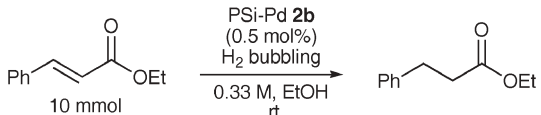
The substrate scope of the hydrogenation was then examined using 0.5 mol% PSi–Pd **2b** in hexane or ethanol under hydrogen gas bubbling conditions at room temperature (Table 2). Alkenes (entries 1, 2), a diene (entry 3), alkynes (entries 4, 9), an α,β -unsaturated ketone (entry 5), and an α,β -unsaturated carboxylic acid (entry 7) were reduced smoothly to afford the desired products in high yields without leaching of Pd. Chalcone also reacted smoothly to give the corresponding ketone and alcohol in 84% and 13% yields, respectively (entry 8). While nitrobenzene was reduced smoothly to afford aniline quantitatively, a small amount of Pd leaching was observed (entry 6). Furthermore, deprotection of a benzyl ether and the benzyloxy-carbonyl group of an amino group also proceeded smoothly with small amounts of Pd leaching (entries 10 and 11). It should be

noted that the catalyst was recovered quantitatively by simple filtration and reused at least five times without leaching of Pd and loss of the catalytic activity (Table 3).

Next, we compared catalytic activity of PSi–Pd **2b** with that of Pd–C and leaching of Pd to the reaction mixture (Table 4). It is noteworthy that the activity of PSi–Pd **2b** was comparable to that of 5% Pd–C, and that leaching of Pd using PSi–Pd was much less than that using 5% Pd–C.

We also conducted Suzuki and Sonogashira reactions using PSi–Pd **2b** (Scheme 1). In both cases, the reactions proceeded smoothly to afford the desired adducts in good yields, and no leaching of Pd was detected.

We then prepared polysilane-supported platinum catalysts (PSi–Pt). After several investigations of platinum sources and

Table 3 Reuse of PSi-Pd **2b**


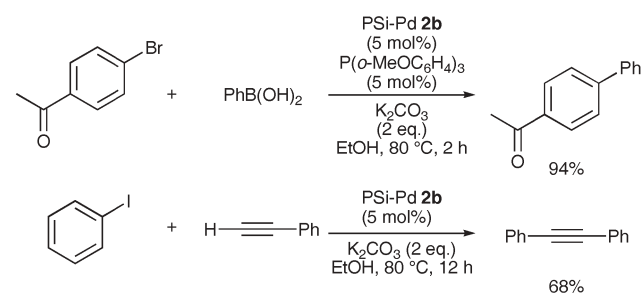
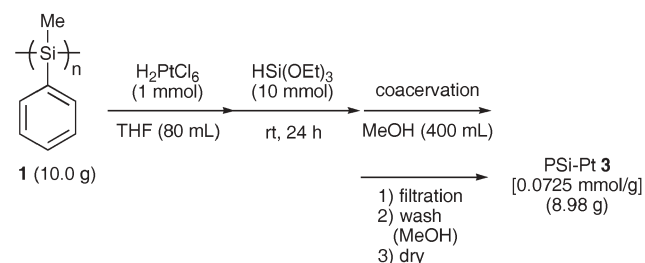
Entry	Run	Conversion (%) ^a	
		10 min	30 min
1	1st	59	>99 ^b
2	2nd	74	>99
3	3rd	77	>99
4	4th	76	>99
5	5th	85	>99

^a Determined by GC analysis. ^b Pd leaching <0.031% by ICP analysis.

Table 4 Comparison between PSi-Pd and Pd-C^a

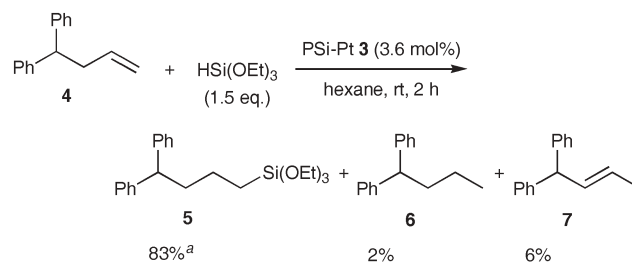
Entry	Pd catalyst	Conversion (%)	Leaching of Pd (%) ^b
1	PSi-Pd 2b	>99	0.023
2	5% Pd-C	>99	0.17

^a Reaction conditions: ethyl cinnamate (10 mmol), Pd catalyst (0.5 mol%), MeOH (30 mL) and H₂ (1 atm), rt, 2 h. The conversions were determined by GC analysis. ^b Determined by ICP analysis.

**Scheme 1** Suzuki and Sonogashira reactions using PSi-Pd **2b**.**Scheme 2** Preparation of PSi-Pt **3**.

reductants, it was revealed that PSi-Pt **3** prepared from hydrogen hexachloroplatinate(IV) hexahydrate and triethoxysilane (Scheme 2) was highly active for hydrosilylation. In the presence of 3.6 mol% of PSi-Pt **3**, 4,4-diphenyl-1-butene (**4**) reacted with triethoxysilane smoothly to afford (4,4-diphenylbutyl)triethoxysilane (**5**) in good yield (Scheme 3).

In summary, we have synthesized immobilized Pd and Pt catalysts based on polysilane for the first time. Polysilane-supported Pd catalysts have been successfully used in hydrogenation. The reactions proceeded in high yields, and the catalysts could be recovered almost quantitatively by simple filtration and reused. Furthermore, no leaching, or a very small amount of leaching of Pd was confirmed by ICP analysis. The Pd catalyst was also used in the Suzuki and Sonogashira reactions.

**Scheme 3** Hydrosilylation using PSi-Pt **3**. ^aA small amount of Pt leaching (0.31%) was detected by ICP analysis. Recovery of PSi-Pt **3**: ca. 90%.

Polysilane-supported Pt catalysts have been prepared by the same method and showed high activity in hydrosilylation. Further investigations to develop other reactions using PSi-Pd and PSi-Pt as well as to prepare other immobilized metal catalysts based on polysilane is now in progress.

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