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

Hidekazu Oyamada, Ryo Akiyama, Hiroyuki Hagio, Takeshi Naito and Shū Kobayashi*

Received (in Cambridge, UK) 17th July 2006, Accepted 28th July 2006 First published as an Advance Article on the web 5th September 2006 DOI: 10.1039/b610241g

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, $Mw = 3.2 \times 10^4$) 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	2а-е
---------	-------------	-----------	------



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.

Science of Process Laboratories, The HFRE Division, ERATO, Japan Science and Technology Agency (JST), Matoba, Kawagoe, Saitama 350-1101, Japan, and Graduate School of Pharmaceutical Sciences, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan. E-mail: skobayas@mol.f.u-tokyo.ac.jp; Fax: +81-3-5684-0634 † Electronic supplementary information (ESI) available: Experimental and TEM images of **2a**, **2b**, and **2f**. See DOI: 10.1039/b610241g

$\underbrace{\text{Substrate}}_{1.0 \text{ mmol}} \xrightarrow{\text{H}_2 \text{ bubbling}}_{\text{hexane (3 mL), rt}} \rightarrow \text{Product}$						
Entry	Substrate	Time/h	Product	Yield (%) ^a	Leaching (%) ^c	
1	0	1	0 	>99 ^b	< 0.08	
	Ph		PhOEt			
2	Ph	2	Ph	97	<0.08	
3	Ph	2	Ph	>99	< 0.08	
4	Ph-Ph	3	Ph	>99	< 0.08	
5		2		>99 ^b	<0.08	
6	NO ₂	1.5	NH ₂	>99 ^b	2.28	
7 ^d	Ph	6	Ph	97	<0.08	
8 ^{<i>d</i>}	Ph	9	Ph Ph (OH Ph Ph Ph Ph	84(13)	<0.08	
9^d	OH	2	Ph	96	< 0.08	
10^d	Ph	10	Ph OH	>99	0.40	
11 ^{<i>d</i>}	Ph N OBn	10	Ph NH ₂	93	5.41	
12 ^d		36		86(9)	0.13	

PSi-Pd 2h (0.5 mol%)

Table 2 PSi-Pd 2b-Catalyzed hydrogenation

^{*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 benzyloxycarbonyl 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 4 Comparison between PSi–Pd and Pd–C^a

Entry	Pd catalyst	Conversion (%)	Leaching of Pd (%) ^k
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. Polysilanesupported 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 Sonogashra reactions.



Scheme 3 Hydrosilylation using PSi–Pt 3. ^{*a*}A 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.

Notes and references

- Reviews: (a) G. W. Parshall and S. D. Ittel, *Homogeneous Catalysis*, Wiley, New York, 1992; (b) *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, Wiley-VCH, Weinheim, 2002.
- 2 Reviews: (a) C. A. McNamara, M. J. Dixon and M. Bradley, *Chem. Rev.*, 2002, **102**, 3275; (b) *Polymeric Materials in Organic Synthesis and Catalysis*, ed. M. R. Buchmeiser, Wiley-VCH, Weinheim, Germany, 2003.
- 3 (a) R. D. Miller and J. Michl, *Chem. Rev.*, 1989, **89**, 1359; (b)
 R. G. Kepler, J. M. Zeigler, L. A. Harrah and S. R. Kurtz, *Phys. Rev. B: Condens. Matter*, 1987, **35**, 2818; (c) M. Abkowitz, F. E. Knier, H. J. Yuh, R. J. Weagley and M. Stolka, *Solid State Commun.*, 1987, **62**, 547; (d) R. West, *J. Organomet. Chem.*, 1986, **300**, 327; (e) H. Suzuki, H. Meyer, J. Simmerer, J. Yang and D. Haarer, *Adv. Mater.*, 1993, **5**, 743.
- 4 (a) H. Suzuki, H. Meyer and S. Hoshino, J. Appl. Phys., 1995, 78, 2684;
 (b) S. Hoshino and H. Suzuki, Appl. Phys. Lett., 1996, 69, 224.
- 5 S. Hayase, Prog. Polym. Sci., 2003, 28, 359.
- 6 D. Seyferth, T. G. Wood, H. J. Tracy and J. L. Robinson, J. Am. Ceram. Soc., 1992, 75, 1300.
- 7 Recently, Sanji *et al.* reported an application of poly[1,1-dimethyl-2,2dihexyldisilene-*b*-poly(methacrylic acid)] to immobilize metal nanoparticles. In this method, however, polysilane is not used as a support for immobilization of metals, but used as a reducing agent of metal ions. T. Sanji, Y. Ogawa, Y. Nakatsuka, M. Tanaka and H. Sakurai, *Chem. Lett.*, 2003, **32**, 980.
- 8 It was reported that transition metal atoms such as Ti, V, Cr, and Mo could be trapped as bis(arene)metal complexes in fluid cyclic oligomers of phenyl-containing polysilane. G. A. Ozin, M. P. Andrews and R. West, *Inorg. Chem.*, 1986, 25, 580.
- 9 Review: (a) S. Kobayashi and R. Akiayam, Chem. Commun., 2003, 449, see also: (b) T. Ishida, R. Akiyama and S. Kobayashi, Adv. Synth. Catal., 2003, 345, 576; (c) T. Ishida, R. Akiyama and S. Kobayashi, Adv. Synth. Catal., 2005, 347, 1189.
- (a) R. Akiyama and S. Kobayashi, J. Am. Chem. Soc., 2003, 125, 3412; 10 (b) K. Okamoto, R. Akiyama and S. Kobayashi, J. Org. Chem., 2004, 69, 2871; (c) K. Okamoto, R. Akiyama and S. Kobayashi, Org. Lett., 2004, 6, 1987; (d) R. Akiyama, T. Sagae, M. Sugiura and S. Kobayashi, J. Organomet. Chem., 2004, 689, 3806; (e) K. Okamoto, R. Akiyama, H. Yoshida, T. Yoshida and S. Kobayashi, J. Am. Chem. Soc., 2005, 127, 2125; (f) H. Hagio, M. Sugiura and S. Kobayashi, Synlett, 2005, 813; (g) S. Kobayashi, H. Miyamura, R. Akiyama and T. Ishida, J. Am. Chem. Soc., 2005, 127, 9251; (h) M. Takeuchi, R. Akiyama and S. Kobayashi, J. Am. Chem. Soc., 2005, 127, 13096; (i) R. Nishio, M. Sugiura and S. Kobayashi, Org. Lett., 2005, 7, 4831; (j) H. Miyamura, R. Akiyama, T. Ishida, R. Matsubara, M. Takeuchi and S. Kobayashi, Tetrahedron, 2005, 61, 12177; (k) H. Hagio, M. Sugiura and S. Kobayashi, Org. Lett., 2006, 8, 375; (1) R. Nishio, M. Sugiura and S. Kobayashi, Org. Biomol. Chem., 2006, 4, 992.