Development of polysilane-supported palladium/alumina hybrid catalysts and their application to hydrogenation

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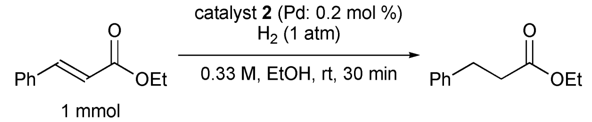
Novel immobilized Pd catalysts, polysilane-supported palladium/alumina hybrid catalysts, have been developed. The catalysts showed high catalytic activity for hydrogenation, and could be used in an organic solvent or under solvent-free conditions.

Palladium is one of the most important hydrogenation catalysts used in both laboratories and industry. While immobilized palladium (Pd) catalysts such as Pd/C and Pd/SiO_2, *etc.* have been often employed, leaching of the palladium from the supports, moderate yields of recovery, contamination of the reaction products with palladium, and poisoning of the catalyst by heteroatoms such as sulfur and nitrogen, *etc.* are sometimes serious problems especially in the manufacture of pharmaceuticals.[1] To address these issues, new methods for the immobilization of homogeneous Pd catalysts onto inorganic or organic supports have been widely investigated.[2] However, tedious procedures are often needed for the preparation of such heterogeneous catalysts, and lower activity/selectivity and leaching of catalysts from the supports remain serious problems.

Previously, we have developed new methods for immobilizing metal catalysts onto polymers, microencapsulation[3] and polymer incarcerated (PI) protocols,[4] which are based on physical envelopment by the polymers, and electronic interaction between π electrons of the benzene rings of the polystyrene-based polymers and vacant orbitals of the metals. Next, we focused on polysilanes as a support for heterogeneous catalysts. Polysilanes have been widely studied due to their interesting electronic properties such as high hole mobility, photoconductivity, and nonlinear optical properties caused by σ-conjugation of the silicon backbone.[5–7] In addition, polysilane is used as a starting material for ceramics and synthetic methods for mass production are established.[8] Recently, we have synthesized immobilized Pd and Pt catalysts based on poly(methylphenyl)silane for the first time.[9] Polysilane-supported Pd catalysts (Pd/PSi) have been successfully used in hydrogenation. The reactions proceeded in high yields, and the catalysts could be recovered and reused almost quantitatively by simple filtration. Polysilane-supported Pt (Pt/PSi) catalysts were prepared by a similar method and showed high activity in hydrosilylation. However, a small amount of Pd leaching was confirmed by ICP analysis when nitrogen-containing compounds such as nitrobenzene were used. Furthermore, these catalysts had a somewhat limited applicability profile, since the carrier polysilane dissolved in some organic solvents. In order to address these issues, we planned to apply the PI method to polysilane-supported catalysts. In this paper, we describe the synthesis of highly active PI Pd/PSi on aluminium oxide and its application to hydrogenation.†

We first examined several metal oxides and the ratio to Pd/PSi for the preparation of hybrid catalysts (Table 1). In a typical procedure, poly(methylphenyl)silane ($M_w = 3.2 \times 10^4$) and $Pd(OAc)_2$ were combined in THF at 0 °C for 1 h, and a metal oxide was added to this mixture. After stirring for a further 1 h, MeOH was added to form microencapsulated Pd (MC Pd/PSi) on the metal oxide. The resulting MC Pd/PSi (**1**) was heated at 140 °C for 2 h, washed sequentially with THF, $CHCl_3$, and MeOH, and dried under reduced pressure to afford PI Pd/PSi on the metal oxide **2**. We tested hybrid catalysts **2** on the hydrogenation of ethyl cinnamate (Scheme 1). When SiO_2 was used, recovery of palladium was low (Table 1, entry 2). On the other hand, Al_2O_3, TiO_2, and ZrO_2 gave promising results (entries 3, 6 and 9). It was found that higher ratios of the metal oxides to Pd/PSi were important for good recovery of palladium and high activity for the hydrogenation (entries 4, 5, 8, 10, and 11).



Scheme 1 Hydrogenation of ethyl cinnamate

Among the metal oxides tested, alumina was revealed to be superior to other metal oxides in terms of yield and quality of the immobilized catalysts (entries 4 and 5). With these data in hand, we further studied preparation conditions of the catalyst using alumina. In a large-scale preparation of PI Pd/PSi, it was found that the heating at 140 °C under neat conditions (cross-linking step) gave low reproducibility, presumably due to irregularity of heating and influence of oxygen. After further investigations, good reproducibility was obtained when decane was used as a solvent under an argon atmosphere. Next, several conditions for the cross-linking step were examined (Table 2). It was found that whilst palladium catalysts **4** that had been prepared at 120 °C and 140 °C for 2 hours gave quantitative conversion in the hydrogenation reaction, those prepared over a longer period of time gave lower conversions in the subsequent hydrogenation (entries 2 and 4). On the other hand, using a preparation temperature of 160 °C even

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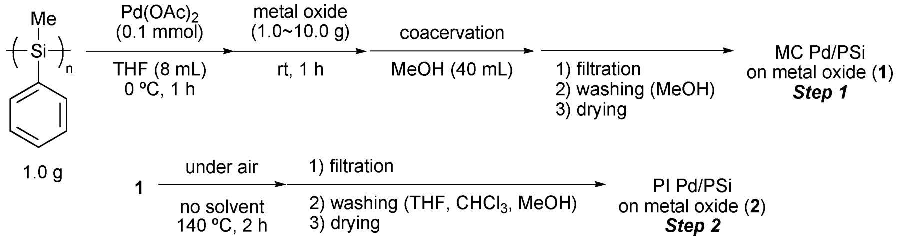
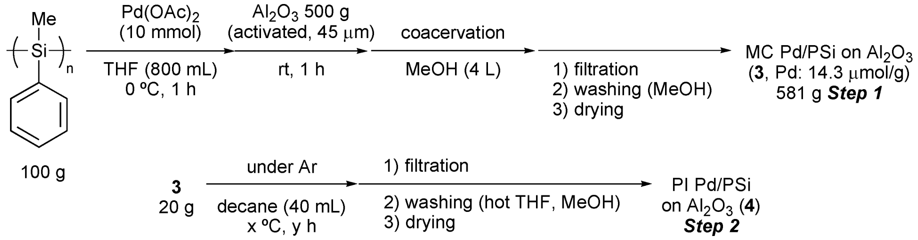
Table 1 Preparation of PI Pd/PSi on metal oxide and hydrogenation reaction



	Preparation of PI Pd/PSi on metal oxide					Hydrogenation[a]	
Entry	Metal oxide (g)	Yield of **1** (g)	Yield of **2**/**1** (w/w)	Loading/μmol g^{-1}	Recovery of Pd (%)[b]	Conversion (%)[c]	Leaching (%)[d]
1	None	0.72	—	13.4	96	94	ND[f]
2	SiO_2 (1.0)	1.81	0.56	49.8	51	88	0.27
3	Al_2O_3 (1.0)	1.63	0.77	72.3	91	55	0.23
4	(5.0)	5.62	0.95	15.1	81	99.8	<0.28
5	(10.0)	10.57	0.96	8.3	85	99.8	<0.28
6	TiO_2 (1.0)	1.63	0.79	60.1	78	74	<0.23
7	(5.0)	5.61	0.99	11.7	65	76	<0.28
8	(10.0)	10.56	0.97	7.3	74	>99.9	<0.28
9	ZrO_2 (1.0)	1.60	0.80	63.7	81	46	<0.23
10	(5.0)	5.61	0.93	16.2	90	99.3	<0.28
11	(10.0)	10.48	0.91	8.2	79	>99.9	<0.30

[a] Reaction conditions: see Scheme 1. [b] Recovery over two steps. [c] Determined by GC analysis. [d] Determined by ICP analysis. [e] MC Pd/PSi was used. [f] Not determined.

Table 2 Preparation of PI Pd/PSi on Al_2O_3 by the heat cross-linking method and hydrogenation reaction



						Hydrogenation[a]		
	Preparation of PI Pd/PSi on Al_2O_3					Conversion (%)[c]		
Entry	x/°C	y/h	Yield of **4**/**3** (w/w)	Loading/μmol g^{-1}	Recovery of Pd (%)[b]	1 h	2 h	Leaching (%)[d]
1	120	2	0.91	15.2	80	94	Quant.	<0.74
2	120	4	0.91	12.7	67	74	93	1.06
3	140	2	0.93	15.8	85	73	Quant.	<0.74
4	140	4	0.93	16.3	89	59	94	<0.74
5	160	2	0.95	15.3	84	63	82	<0.74

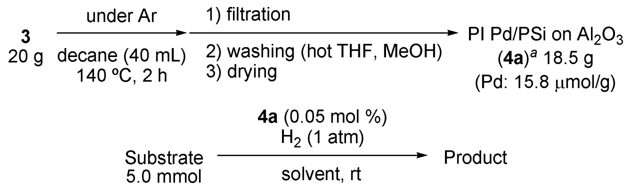
[a] Reaction conditions: ethyl cinnamate (1 mmol), Pd catalyst **4** (0.1 mol%), EtOH (1 mL) and H_2 (1 atm), rt, 2 h. [b] Recovery of two steps. [c] Determined by GC analysis. [d] Determined by ICP analysis.

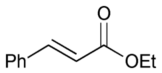
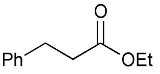
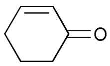
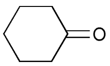
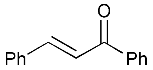
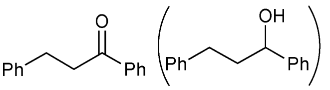
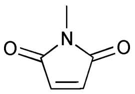
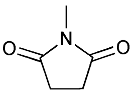
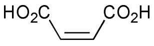
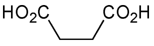
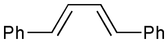
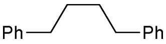
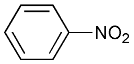
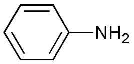
over the shortened time of 2 hours only afforded a catalyst whose activity was comparatively low (entry 5).

The substrate scope of the hydrogenation was then examined using 0.05 mol% PI Pd/PSi on alumina (**4a**) in organic solvents such as ethanol and dichloromethane under hydrogen gas at atmospheric pressure and room temperature (Table 3). Gratifyingly it was found that under these conditions ethyl cinnamate (entry 1) and 2-cyclohexen-1-one (entry 2) were reduced smoothly in EtOH to afford the desired products in high yields without leaching of Pd. Chalcone also reacted smoothly to give the corresponding ketone and alcohol in 91% and 6% yields, respectively (entry 3). While *N*-methylmaleimide, maleic acid, and a diene were reduced smoothly to afford *N*-methylsuccinimide, succinic acid, and alkane in high yields, respectively, a small amount of Pd leaching was observed (entries 4, 5 and 6). Furthermore, in the case of using catalyst **4a**, nitrobenzene was reduced smoothly to afford aniline quantitatively. It is particularly noteworthy that the leaching of Pd in this instance was lower than that observed when using the MC Pd/PSi catalyst (entries 7 and 8).

We also evaluated catalyst **4a** in the hydrogenation of ethyl cinnamate, *N*-methylmaleimide, and chalcone using 0.05 or 0.20 mol% of Pd under solvent-free conditions (Table 4).[10] We

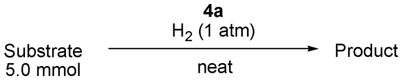
Table 3 Substrate scope

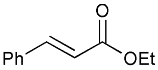
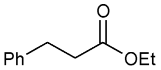
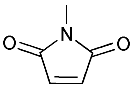
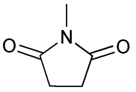
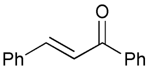
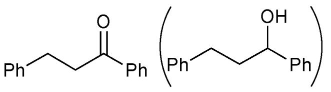


Entry	Substrate	Solvent	Conc./mol L^{-1}	Time/h	Product	Yield (%)[b]	Leaching (%)[c]
1		EtOH	0.33	1		>99.9[d]	<0.22
2		EtOH	1.0	4		Quant.	<0.30
3		EtOH	1.0	24		91 (6)	0.99
4		EtOH	0.50	1		97	0.48
5		EtOH	1.0	3.5		Quant.	0.94
6		CH_2Cl_2	0.50	24		98	3.6
7		EtOH	1.0	8		>99.9[d]	0.34
8[e]		Hexane	0.33	1.5		>99.9[d]	2.28

[a] Pd: 0.142 wt%, Al: 47.7 wt%, Si: 2.28 wt% (determined by ICP analysis). [b] Determined by ^1H NMR analysis. [c] Determined by ICP analysis. [d] Conversion, determined by GC analysis. [e] 0.50 mol% of MC Pd/PSi without Al_2O_3 was used. See ref. 9

Table 4 Hydrogenation without solvent



Entry	Substrate	4a/mol%	Temp.	Time/h	Product	Yield (%)[a]	Leaching (%)[b]
1		0.05	RT	8		>99.9[c]	<0.22
2[d]		0.05	50 °C	16		Quant.[e]	<0.10
3		0.05	50 °C	1		58	—
4		0.20	RT	1		79	—
5		0.05	50 °C	24		80 (Trace)	—
6		0.20	50 °C	24		95 (5)	0.12

[a] Determined by ^1H NMR analysis. [b] Determined by ICP analysis. [c] Conversion, determined by GC analysis. [d] 25 mmol scale. [e] Determined by GC analysis

had previously found that when using MC Pd/PSi with a liquid chemical such as ethyl cinnamate as substrate, the catalyst was dissolved in the substrate and the palladium metal tended to leach from the support. Pleasingly however, it was discovered that in the case of **4a**, the reaction could be conducted without leaching of Pd (entries 1 and 2). Solid chemicals such as *N*-methylmaleimide and chalcone could be used as substrates directly and good chemical yields were obtained (entries 3, 4, 5 and 6). Particularly, in the case of chalcone, it is noted that the leaching of Pd was lower than that observed when using ethanol as a solvent (entry 6, *cf.* Table 3, entry 3).

In order to probe the structure of the catalyst, we analyzed PI catalyst **4** (Table 2, entry 3) by ^{29}Si CPMAS NMR (Fig. 1). In the preparation of MC Pd/PSi on alumina (**3**), while a portion of the Si–Si bonds were oxidized to form O–Si–O bonds, almost the same signals (chart c) as for those of poly(methylphenylsilane) (chart a) were observed. On the other hand, PI Pd/PSi on alumina [catalyst **4** (Table 2, entry 3)] gave interesting spectra (chart d). ^{29}Si NMR analysis revealed four signals at about −100, −40, −33, and −25 ppm, corresponding to Si–O–Al, Si–Si, O–Si–O, and Si–O–Si bonds, respectively. It was assumed that polysilane was fixed on activated alumina by formation of linkages with aluminium through oxygen. In addition, since alumina has a lot of nanopores on the surface, it is expected that the polysilane-supported palladium clusters are included in these nanopores and stabilized. However, at the current time the precise structure of catalyst **4** is still unclear, and further investigation and information are needed.

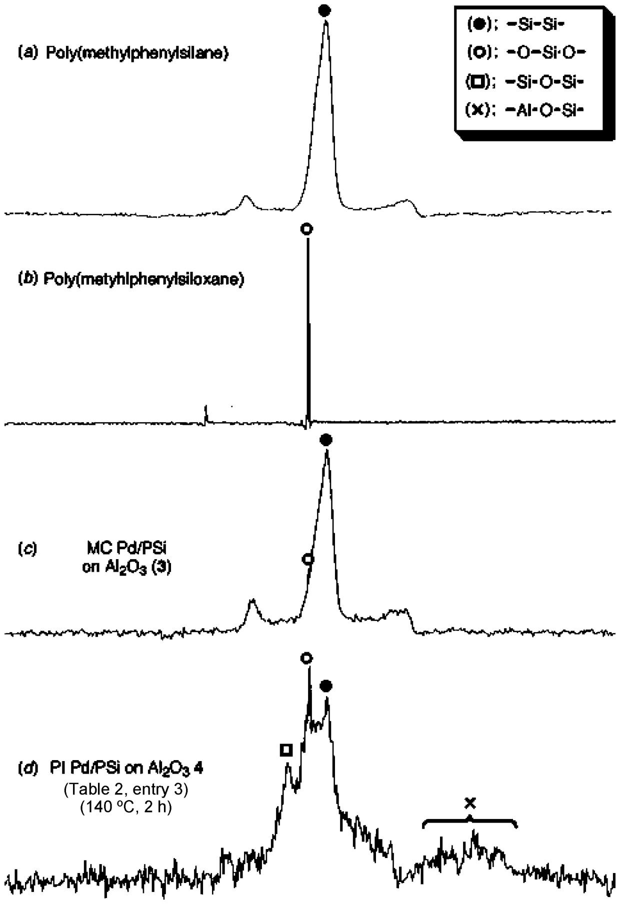


Fig. 1 Comparison of ^{29}Si CPMAS NMR spectra

In summary, we have developed novel polysilane-supported palladium/alumina hybrid catalysts. These catalysts showed high catalytic activity in hydrogenation and could be used in an organic solvent or under solvent-free conditions. Further investigations to prepare other immobilized metal catalysts as well as their applications to other reactions are now in progress.[11]

Notes and references

† **Synthesis of poly(methylphenylsilane):** Methylphenyldichlorosilane (382 g, 2.00 mol) was added dropwise to a suspension of sodium (96.6 g, 4.20 mol) in THF (1 L) over 30 min with vigorous stirring at reflux temperature. After stirring for further 3.5 h, the mixture was cooled in an ice bath and diluted with toluene (500 mL). 3 N HCl (500 mL) was added dropwise to the mixture, the organic layer was separated, and water was added to the aqueous layer to dissolve NaCl. The aqueous layer was extracted with toluene and the combined organic layers were washed with H_2O, 5% aqueous solution of $NaHCO_3$, H_2O and brine. The organic layer was dried over Na_2SO_4 and concentrated to *ca.* 600 mL *in vacuo*. MeOH (750 mL) was added to the solution, the precipitate was collected by filtration and washed with MeOH. The crude polysilane was dissolved in toluene (370 mL) and precipitated by adding *i*PrOH. The precipitate was collected, washed with toluene–*i*PrOH (1 : 5) and dried under reduced pressure at 55 °C to afford poly(methylphenylsilane) (135 g, 56% yield). $M_w = 3.21 \times 10^4$, $M_n = 1.12 \times 10^4$, $M_w/M_n = 2.87$.
General procedure for the preparation of PI Pd/PSi on Al_2O_3 (4) (Table 2): Poly(methylphenylsilane) (100 g) was dissolved in THF (800 mL) and cooled to 0 °C. To this solution, palladium(II) acetate (2.25 g, 10.0 mmol) was added and the mixture was stirred for 1 h at this temperature. To the dark brown polymer solution was added alumina (500 g), and the mixture was allowed to warm to room temperature. After 2 h, MeOH (4 L) was slowly added for coacervation and the resulting precipitate was collected by filtration, washed with MeOH several times and dried under reduced pressure at 55 °C to afford the microencapsulated palladium catalyst (MC Pd/PSi on Al_2O_3 **3**, 581 g, Pd = 14.3 mmol g^{-1}, 83% of Pd was loaded). The Pd loading was determined by ICP analysis. MC catalyst **3** (20 g) was suspended in decane (40 mL) at room temperature, and heated to 120–160 °C for 2–4 h. The resulting solid was collected by filtration, washed with hot THF and MeOH several times and dried under reduced pressure at 55 °C. The polymer incarcerated palladium catalysts (PI Pd/PSi on Al_2O_3 **4**) were obtained. The loading of Pd was determined by ICP analysis.
Hydrogenation catalyzed by PI Pd/PSi on Al_2O_3 (4a) (Table 3): A typical experimental procedure is described for the hydrogenation of ethyl cinnamate. Ethyl cinnamate (5 mmol) and PI Pd/PSi on Al_2O_3 (**4a**, 0.05 mol%) were combined in ethanol (15 mL). The mixture was stirred for 1 h at room temperature under H_2 atmosphere (1 atm). The yield and conversion were determined by GC analysis with reference to naphthalene or ^{1}H NMR analysis with reference to 1,2,3,4-tetramethylbenzene (durene) as an internal standard. The leaching of Pd from the support was determined by ICP analysis.

1 (*a*) D. L. Trimm, *Design of Industrial Catalysts*, Elsevier, Amsterdam, 1980; (*b*) P. N. Rylander, *Hydrogenation Methods*, Academic Press, New York, 1985; (*c*) C. N. Satterfield, *Heterogeneous Catalysis in Industrial Practice*, McGraw-Hill, New York, 2nd edn, 1991.
2 (*a*) C. A. McNamara, M. J. Dixon and M. Bradley, *Chem. Rev.*, 2002, **102**, 3275–3300; (*b*) *Polymeric Materials in Organic Synthesis and Catalysis*, ed. M. R. Buchmeiser, Wiley-VCH, Weinheim, Germany, 2003.
3 (*a*) S. Kobayashi and R. Akiyama, *Chem. Commun.*, 2003, 449–460; (*b*) T. Ishida, R. Akiyama and S. Kobayashi, *Adv. Synth. Catal.*, 2003, **345**, 576–579; (*c*) T. Ishida, R. Akiyama and S. Kobayashi, *Adv. Synth. Catal.*, 2005, **347**, 1189–1192.
4 (*a*) R. Akiyama and S. Kobayashi, *J. Am. Chem. Soc.*, 2003, **125**, 3412–3413; (*b*) K. Okamoto, R. Akiyama and S. Kobayashi, *J. Org. Chem.*, 2004, **69**, 2871–2873; (*c*) K. Okamoto, R. Akiyama and S. Kobayashi, *Org. Lett.*, 2004, **6**, 1987–1990; (*d*) R. Akiyama, T. Sagae, M. Sugiura and S. Kobayashi, *J. Organomet. Chem.*, 2004, **689**, 3806–3809; (*e*) K. Okamoto, R. Akiyama, H. Yoshida, T. Yoshida and S. Kobayashi, *J. Am. Chem. Soc.*, 2005, **127**, 2125–2135; (*f*) H. Hagio, M. Sugiura and S. Kobayashi, *Synlett*, 2005, 813–817; (*g*) S. Kobayashi, H. Miyamura, R. Akiyama and T. Ishida, *J. Am. Chem. Soc.*, 2005, **127**, 9251–9254; (*h*) M. Takeuchi, R. Akiyama and S. Kobayashi, *J. Am. Chem. Soc.*, 2005, **127**, 13096–13097; (*i*) R. Nishio, M. Sugiura and S. Kobayashi, *Org. Lett.*, 2005, **7**, 4831–4834; (*j*) H. Miyamura, R. Akiyama, T. Ishida, R. Matsubara, M. Takeuchi and S. Kobayashi, *Tetrahedron*, 2005, **61**,

12177–12185; (*k*) R. Nishio, S. Wessely, M. Sugiura and S. Kobayashi, *J. Comb. Chem.*, 2006, **8**, 459–461; (*l*) H. Hagio, M. Sugiura and S. Kobayashi, *Org. Lett.*, 2006, **8**, 375–378; (*m*) R. Nishio, M. Sugiura and S. Kobayashi, *Org. Biomol. Chem.*, 2006, **4**, 992–995; (*n*) H. Miyazaki, H. Hagio and S. Kobayashi, *Org. Biomol. Chem.*, 2006, **4**, 2529–2531; (*o*) H. Miyamura, R. Matsubara, Y. Miyazaki and S. Kobayashi, *Angew. Chem., Int. Ed.*, 2007, **46**, 4151–4155; (*p*) T. Matsumoto, M. Ueno, J. Kobayashi, H. Miyamura, Y. Mori and S. Kobayashi, *Adv. Synth. Catal.*, 2007, **349**, 531–534.

5 (*a*) R. D. Miller and J. Michl, *Chem. Rev.*, 1989, **89**, 1359–1410; (*b*) R. G. Kepler, J. M. Zeigler, L. A. Harrah and S. R. Kurtz, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1987, **35**, 2818–2822; (*c*) M. Abkowitz, F. E. Kneier, H.-J. Yuh, R. J. Weagley and M. Stolka, *Solid State Commun.*, 1987, **62**, 547–550; (*d*) R. West, *J. Organomet. Chem.*, 1986, **300**, 327–346; (*e*) H. Suzuki, H. Meyer, J. Simmerer, J. Yang and D. Haarer, *Adv. Mater.*, 1993, **5**, 743–746.

6 (*a*) H. Suzuki, H. Meyer and S. Hoshino, *J. Appl. Phys.*, 1995, **78**, 2684–2690; (*b*) S. Hoshino and H. Suzuki, *Appl. Phys. Lett.*, 1996, **69**, 224–226.

7 S. Hayase, *Prog. Polym. Sci.*, 2003, **28**, 359–381.

8 D. Seyferth, T. G. Wood, H. J. Tracy and J. L. Robison, *J. Am. Ceram. Soc.*, 1992, **75**, 1300–1302.

9 H. Oyamada, R. Akiyama, H. Hagio, T. Naito and S. Kobayashi, *Chem. Commun.*, 2006, 4297–4299.

10 (*a*) K. Tanaka and F. Toda, *Solvent-free Organic Synthesis*, Wiley-VCH, Weinheim, 2003; (*b*) *Supported Reagents and Catalysts in Chemistry*, ed. B. K. Hodnett, A. P. Kybett, J. H. Clark and K. Smith, The Royal Society of Chemistry, Cambridge, 1998; (*c*) *Solid Supports and Catalyst in Organic Synthesis*, ed. K. Smith, Ellis Horwood Limited, New York, 1992.

11 The reusability of the catalyst has not been determined and will be also the subject of future study.