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COMMUNICATION

Palladium-supported ionic liquid catalyst (Pd-SH-SILC) immobilized on mercaptopropyl silica gel as a chemoselective, reusable and heterogeneous catalyst for catalytic hydrogenation†

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Palladium acetate was immobilized as Pd-SH-SILC (Pd-supported ionic liquid catalyst) in the pores of amorphous mercaptopropyl silica gel with the aid of an ionic liquid [bmim]BF_4. The heterogeneous Pd-SH-SILC was effective for catalytic hydrogenation of a variety of olefins at atmospheric pressure and room temperature. It withstood recycling up to 10 times by decantation.

Catalytic hydrogenation is one of the most fundamentally important synthetic transformations both in the laboratory and in industry. More active, mild, selective and environmentally benign protocols are continuously being sought. Although homogeneous catalysts exhibit higher, more selective catalytic activity, they lack stability and recyclability. One way to improve recyclability is to immobilize a homogeneous catalyst in a liquid support; this can be done by simply dissolving a known homogeneous catalysts in the liquid.

Ionic liquids have attracted considerable interest as liquid supports for homogeneous catalysts, because of they are non-lipophilic, non-hydrophilic, non-volatile and non-coordinating and are capable of dissolving highly ionic substances.[1] Catalytic hydrogenations in ionic liquids have been extensively investigated with a variety of homogeneous catalysts,[2] and have reaction rates greater than those of conventional solvent.[3]

However, catalytic reactions in ionic liquids suffer from high cost and the laborious extraction of the product from the viscous ionic liquid. To solve these issues, SILC (supported ionic liquid catalyst) immobilization was designed to confine the homogeneous catalyst in an ionic liquid to the pores of an amorphous solid.[1,4] SILC immobilization transforms the homogeneous catalyst into a heterogeneous catalyst, and converts the pores of the amorphous solid into micro reaction vessels, allowing straightforward separation of the catalyst and product by filtration and recycling of the catalyst.

A variety of SILCs for catalytic hydrogenation have been reported in combination with various catalysts, ionic liquids and solid supports: Rh/[bmim]PF_6/silica gel,[4a] Pd/guanidium lactate/molecular sieves,[4c] porous Ni/[bmim][n-$C_8H_{17}OSO_3$],[4h] Rh/[bmim]PF_6/carbon nanotubes,[4i] and Pd/[bmim]PF_6/carbon cloth.[4k] However, in most cases, the hydrogenations were carried out under high pressure, the substrates were simple olefins with no functional groups, and some SILCs lacked recyclability.

As a part of our ongoing efforts to immobilize homogeneous catalysts as SILCs,[5] we immobilized palladium acetate as a pre-catalyst with an ionic liquid as the supporting liquid layer in the pores of an amorphous reversed-phase silica gel. The heterogeneous catalyst thus prepared (Pd-SH-SILC) exhibited higher general and chemoselective catalytic activity, and was also recyclable (Fig. 1).

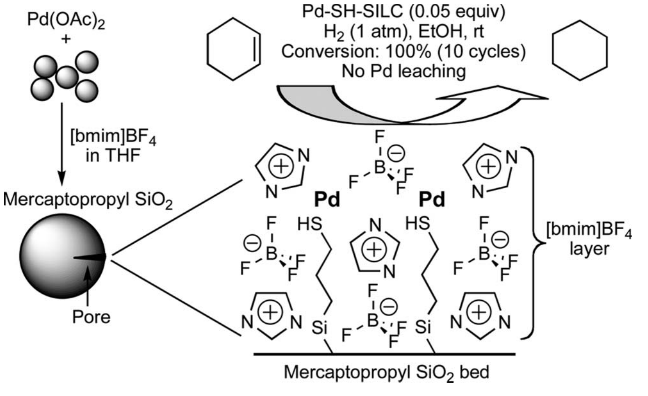

Fig. 1 Catalytic hydrogenation by Pd-SH-SILC.

Immobilization of palladium acetate was carried out according to the procedure described in our previous papers (Fig. 1).[5a–c] A suspension of silica gel in a solution of palladium acetate and the ionic liquid was stirred until the orange color of the solution was transferred to the silica gel. After evaporation of the solvent, an orange free-flowing powder was obtained. Of the silica gels, mercaptopropyl silica gel (sulfur content: 0.67 mmol g^{-1}) was

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† Electronic supplementary information (ESI) available: SEM images of Pd-SH-SILC and GC charts. See DOI: 10.1039/c1gc15217c

Table 1 Optimization of solid support and ionic liquid for the immobilization of palladium acetate

Entry	Support material	Ionic liquid	Abbreviation	Loading of Pd (mmol g^{-1})
1	Mercaptopropyl SiO$_2$	[bmim]PF$_6$	Pd-SH-SILC	0.50
2		[bmim]BF$_4$		0.51
3		—		0.53
4[a]		[bmim]NTf$_2$		0.43
5	Aminopropyl SiO$_2$	[bmim]PF$_6$	Pd-NH$_2$-SILC	0.32
6	Diethylaminopropyl SiO$_2$		Pd-NEt$_2$-SILC	0.30
7	SiO$_2$		Pd-SILC	0.25

[a] The ionic liquid was not confined in the pores of the silica gel.

found to immobilize a sufficient amount of palladium acetate in the presence or absence of an ionic liquid (Table 1, entries 1~3). The higher uptake of palladium acetate in mercaptopropyl silica gel than normal silica gel might be partly because the mercapto group has a better affinity for palladium.[6] Whereas palladium acetate was absorbed into the mercaptopropyl silica gel, [bmim]NTf$_2$ was not confined to the pores (Table 1, entry 4). Mercaptopropyl silica gel has already been used as a scavenger of metal ions[7] and as a solid support for Cu-SILC.[5e] Palladium immobilized in mercaptopropyl mesoporous silica gel was also found to be effective as a heterogeneous catalyst for Mizoroki–Heck and Suzuki–Miyaura reactions by Shimizu[7a] and Crudden,[7b] respectively. Mercaptopropyl silica gel can be prepared by grafting mercaptopropyl trimethoxysilane on to normal silica gel.

The hydrogenation of cyclohexene was used as a benchmark reaction to investigate the catalytic performance of a variety of Pd-SILCs (Table 2). The Pd-SILC immobilized in the pores of mercaptopropyl silica (Pd-SH-SILC) using [bmim]PF$_6$ exhibited comparable catalytic performance to Pd/C (Table 2, entry 2). Moreover, pre-treatment of the Pd-SH-SILC under a hydrogen atmosphere resulted in black powder due to the formation of Pd(0), which was more active (Table 2, entries 6 and 7) than the other pre-treatments (Table 2, entries 8 and 9). Pd-SH-SILC immobilized with [bmim]BF$_4$ exhibited the best catalytic performance (Table 2, entry 7). This result might be because the molecular hydrogen is four times more soluble in [bmim]BF$_4$ than in [bmim]PF$_6$.[8] The activity of the reduced Pd-SH-SILC was maintained for more than 3 months when kept at room temperature under nitrogen. Despite its higher catalytic activity, the reduced Pd-SH-SILC did not ignite even after prolonged exposure to air.

Table 2 Optimization of Pd-SILC for the catalytic hydrogenation of cyclohexene

Entry[a]	Pd-SILC[b]	Time (min)	Conversion (%)[c]
1	Pd/C	120	100
2	Pd-SH-SILC		100
3	Pd-NEt$_2$-SILC		88
4	Pd-SILC		63
5	Pd-NH$_2$-SILC		46
6[d]	Pd-SH-SILC	70	100
7[d,e]		70	100
8[f]		100	100
9[g]		150	100

[a] Reaction carried out in ethanol at atmospheric pressure at 25 °C with 0.05 eq. of Pd-SILC. [b] Immobilized with [bmim]PF$_6$. [c] Determined by GC with toluene as an internal standard. [d] Pd-SILC was reduced with hydrogen in ethanol for 5 h before use. [e] Immobilized with [bmim]BF$_4$. [f] Pd-SILC was placed in ethanol for 18 h before use. [g] Pd-SILC was heated at reflux in *n*-hexane for 21 h before use.

Pd-SH-SILC could be recycled up to 10 times by decantation, while maintaining a 100% conversion with virtually no loss of reactivity (Table 3, entries 1 and 2). The activity of Pd-SH-SILC immobilized with the aid of [bmim]BF$_4$ was found to best withstand recycling (Table 3, entry 1).[9] It is interesting to note that all subsequent recycle experiments carried out in Table 3, entry 1, terminated in 40~50 min as the result of activation of Pd-SH-SILC in the initial hydrogenation. Although palladium acetate could also be immobilized on mercaptopropyl silica without an ionic liquid, its catalytic activity was reduced (Table 3, entry 3).

The leaching of palladium from the Pd-SH-SILC was below the limit of detection for ICP-AES analysis in the reduction of cyclohexene using 0.05 eq. of Pd-SH-SILC. The turnover number (TON) for Pd-SH-SILC was evaluated as 40,000 and the turnover frequency (TOF) was found to be 555 h^{-1}.

The catalytic performance of Pd-SH-SILC immobilized with [bmim]BF$_4$ was general to a variety of olefinic substrates (Table 4).[10] Allylic alcohol was reduced without accompanying hydrogenolysis[11] (Table 4, entry 1), and acid or base sensitive protecting groups were not de-protected (Table 4, entries 2 and 3). Furthermore, the benzyl ether protecting group was left intact under these reaction conditions, even for prolonged reaction times (Table 4, entry 5). Similarly, the Cbz group remained intact (Table 4, entry 6), when ethyl acetate was used as solvent.[12] Aryl bromide was not reduced (Table 4, entry 7),[13] and a single stereoisomer with a *trans*-ring juncture was obtained (Table 4, entry 8).[14] α,β-Unsaturated aldehydes were reduced in quantitative yield without further reduction to primary alcohols or formation of acetals (Table 4, entries 9 and 10). Moderate yields are because of the volatile nature

Table 3 Effect of ionic liquid on catalytic performance of Pd-SH-SILC in hydrogenation of cyclohexene in 10 cycles

Entry[a]	Ionic liquid	Average reaction time (min)
1	[bmim]BF$_4$	45
2	[bmim]PF$_6$	80
3	—	60

[a] Reaction was carried out in ethanol at atmospheric pressure and room temperature with 0.05 equiv of Pd-SH-SILC until 100% conversion.

Table 4 Catalytic performance of Pd-SH-SILC for hydrogenation

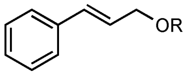
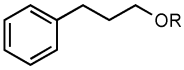
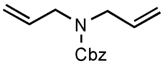
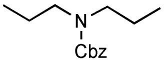
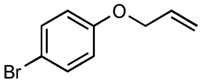
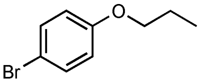
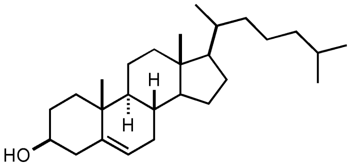
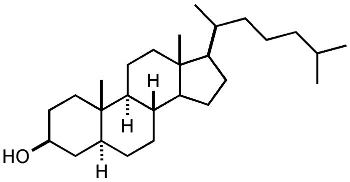
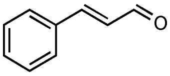
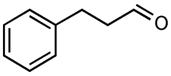
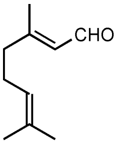
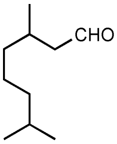
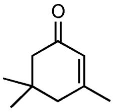
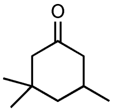
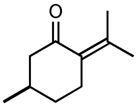
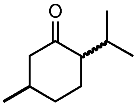
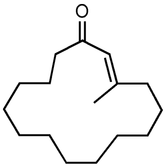
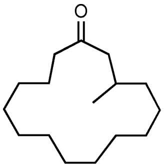
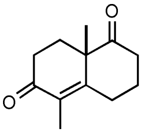
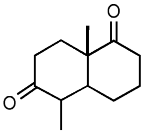
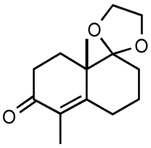
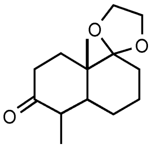
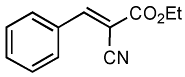
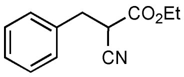
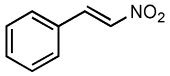
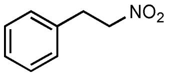
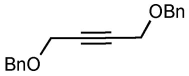
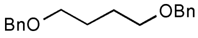
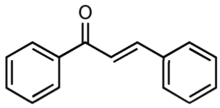
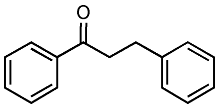
Entry[a]	Olefin **1**	Product **2**	Time (h)	Yield (%)[a]
1	 R = H **1a**	 R = H **2a**	2	100
2	R = Ac **1b**	R = Ac **2b**	0.5	97
3	R = TBS **1c**	R = TBS **2c**	0.5	96
4	R = Bn **1d**	R = Bn **2d**	0.5	97
5	R = Bn **1d**	R = Bn **2d**	0.5	97
6[c]	 **1e**	 **2e**	24	99
7	 **1f**	 **2f**	1	94
8	 **1g**	 **2g** (single isomer)	5	72
9	 **1h**	 **2h**	5	78
10	 **1i**	 **2i**	3	86
11	 **1j**	 **2j**	5	100
12	 **1k**	 **2k** (1:1 diastereomeric mixture)	5	86
13	 **1l**	 **2l**	0.5	99
14	 **1m**	 **2m** (mixture of diastereomers)	2	100
15	 **1n**	 **2n** (mixture of diastereomers)	5	84

Table 4 *(Contd.)*

Entry[a]	Olefin **1**	Product **2**	Time (h)	Yield (%)[a]
16	 **1o**	 **2o**	1	98
17	 **1p**	 **2p**	24	82
18	 **1q**	 **2q**	0.5	94
19	 **1r**	 **2r**	2	82

[a] Reaction was carried out in ethanol at atmospheric pressure and room temperature with 0.05 eq. of Pd-SH-SILC, which was immobilized with [bmim]BF_4, reduced with hydrogen in ethanol for 5 h before use and stored at room temperature under nitrogen. [b] Isolated pure product after MPLC purification. [c] Ethyl acetate was used as the solvent.

of products during purification. These results show Pd-SH-SILC is a mild and selective catalyst, which could be applied to the hydrogenation of a variety of olefinic substrates with a wide range of functional groups. Moreover, tetrasubstituted α,β-unsaturated carbonyl compounds were reduced at atmospheric pressure (Table 4, entries 11, 13 and 14), which verifies the superior catalytic activity of Pd-SH-SILC. In contrast to the hydrogenation of pulegone catalyzed by Pd/C, thymol was not a by-product when Pd-SH-SILC was used (Table 4, entry 12).[15] The acetylenic bond was also smoothly hydrogenated (Table 4, entry 18), and the carbonyl group of chalcone remained intact (Table 4, entry 19).[13]

There are two published examples of hydrogenation by heterogeneous palladium catalysts poisoned by sulfur. Sajiki *et al.* used Pd/C poisoned with diphenylsulfide to give chemoselective hydrogenation at room temperature and atmospheric pressure, in which a variety of olefins were reduced leaving benzyl ether, benzyl ester or *N*-Cbz protecting groups intact.[13] Rossi *et al.* reported the catalytic hydrogenation of cyclohexene by palladium on iron nanoparticles grafted with mercaptopropionic acid at 75 °C under 10 atm of hydrogen.[16] However, Pd-SH-SILC exhibited improved catalytic performance along with better recyclability.

In summary, palladium acetate was immobilized as Pd-SH-SILC in the pores of amorphous mercaptopropyl silica gel with the ionic liquid [bmim]BF_4. The immobilization procedure was simple and cost effective without employing synthetic transformations or a large amount of costly ionic liquid. The reduced Pd-SH-SILC exhibited higher, more selective catalytic activity at room temperature under atmospheric pressure, and could be recycled up to 10 times by simple decantation, while maintaining 100% conversions. The protocol we report herein may be suitable for liquid-phase hydrogenation of substrates, especially those of higher molecular weight, those with multifunctional groups, or for process or industrial-scale applications.

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10 Catalytic hydrogenation of cinnamyl alcohol: A suspension of cinnamyl alcohol (54 mg, 0.4 mmol) and Pd-SH-SILC (40 mg, 0.02 mmol) in EtOH (4 mL) was stirred under hydrogen at room temperature for 2 h. After centrifugation, the organic layer was separated by decantation and the flask was rinsed with ether. The combined organic layers were evaporated to dryness *in vacuo*. The residue was purified by column chromatography (eluent: *n*-hexane–ethyl acetate = 3 : 1) and subsequently by medium pressure LC (eluent: *n*-hexane–ethyl acetate = 6 : 1) to give 3-phenylpropanol (55 mg, quant.).

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