

Selective Hydrogenation of Alkenes under Ultramild Conditions

Valerica Pandarus,[†] Genevieve Gingras,[†] François Béland,^{*,‡} Rosaria Ciriminna, and Mario Pagliaro^{*,‡}[†]SiliCycle Inc., 2500 Parc-Technologique Blvd, Quebec City, Quebec, Canada G1P 4S6[‡]Istituto per lo Studio dei Materiali Nanostrutturati, CNR, via U. La Malfa 153, 90146 Palermo, Italy

ABSTRACT: SiliaCat Pd⁰ solid catalyst heterogeneously mediates at room temperature the selective hydrogenation of a wide variety of alkenes under hydrogen balloon conditions using a modest 0.1 mol % catalyst amount. The catalyst is recyclable with negligible leaching of valued palladium, providing the chemical industry with a suitable replacement for less selective metal-based catalysts.

1. INTRODUCTION

Catalytic hydrogenation of unsaturated C–C bonds either under homogeneous¹ or heterogeneous² conditions is the method of choice to perform one of the fundamental reactions in organic chemistry. Catalysis, where possible, is generally preferred to noncatalytic chemical methods.³ Homogeneous catalysts in general exhibit high activity and selectivity with special application in asymmetric catalysis, although they are often expensive and their separation and reuse is troublesome. When possible, namely when selective activity is sufficient and leaching has been minimized, heterogeneous catalysis is preferred over homogeneous processes as solid catalysts are easy to separate and reuse, minimize the presence of metal residues in the product, improve the handling and process control and, therefore, reduce the overall process costs. Usually, the heterogeneous hydrogenation is carried out finely divided supported metals (Pt, Pd, Rh, Ir, Ru, and Ni). Nonsupported metal (Fe) nanoparticles at the frontier between homogeneous and heterogeneous catalysis are also being developed.⁴

Most palladium heterogeneous catalysts (commercial Pd/C, nanoparticles,⁵ colloidal palladium species,⁶ and polymer-incarcerated palladiums⁷) may show palladium leaching, low reactivity and rapid degradation.⁸

SiliaCat Pd⁰ is an organoceramic matrix entrapping ultrasmall Pd(0) nanocrystallites, whose selective activity in the hydrogenation of functionalized nitroarenes under mild conditions has already been reported.⁹ To the best of our knowledge, the most efficient performing palladium catalyst for alkenes hydrogenation is made of nanoparticles in polystyrene normally requiring 0.5 mol % catalyst at room temperature to afford hydrogenated products in high yield.¹⁰ It is thus of relevant interest the discovery reported herein concerning the catalytic activity of new SiliaCat Pd(0) heterogeneous catalysts for the hydrogenation reaction of a series of olefins compounds under remarkably mild conditions, namely at room temperature with 1 bar H₂ in a simple hydrogen balloon, using a modest 0.1 mol % catalyst amount.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. SiliaCat Pd⁰ is made of highly dispersed Pd nanoparticles (uniformly in the range 4.0–6.0 nm) encapsulated within an organosilica matrix via an alcohol-free sol–gel process typical of enzyme sol–gel encapsulation.

We have described in detail elsewhere⁸ its preparation. The SiliaCat Pd⁰ catalyst used in all the catalytic experiments described below has a Pd load = 0.05 mmol/g measured using the CAMECA SX100 instrument equipped with EPMA analyzer.

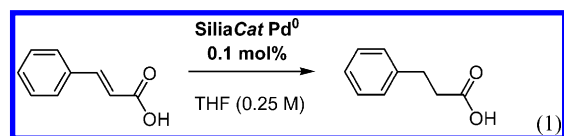


Table 1. Influence of the solvent on catalytic activity of SiliaCat Pd⁰ heterogeneous catalyst in hydrogenation reaction of 1-decene and 1-octadecene^a

entry	substrate	catalyst (mol %)	solvent ^b (M)	time (h)	conv. (yield) ^c (%)
1	1-decene	0.1	MeOH (0.2 M)	0.5	80
				1	97
2	1-decene	0.1	MeOH (0.25 M)	0.5	100
3	1-decene	0.1	MeOH (0.3 M)	0.5	98
				1	100
4	1-decene	0.1	EtOH (0.25 M)	1	75
				2	100
5	1-decene	0.1	THF (0.25 M)	1	85
				2	98
6	1-decene	0.1	EtOAc (0.25 M)	1	95
				2	100
7	1-decene	0.1	hexane (0.25 M)	0.5	98
				1	100
8	1-octadecene	0.1	MeOH/THF(4:1) (0.2 M)	0.5	100 (99.6)
9	1-octadecene	0.1	MeOH/THF(4:1) (0.25 M)	0.5	100 (99.7)
11	1-octadecene	0.1	MeOH/THF(4:1) (0.3 M)	0.5	100 (99.4)
12	1-octadecene	0.1	MeOH/THF(4:1) (0.5 M)	0.5	99 (98.7)
13	1-octadecene	0.1	MeOH/THF(1:1) (0.5 M)	0.5	100 (99)
14	1-octadecene	0.1	MeOH/THF(1:4) (0.5 M)	0.5	98
15	1-octadecene	0.1	THF (0.5 M)	1	95

^aExperimental conditions: 6 mmol substrate in HPLC grade solvent and 0.1 mol % SiliaCat Pd⁰ catalyst under hydrogen balloon room temperature conditions. ^bMolar concentration in respect to the substrate. ^cEvaluated by GC/MS analysis. Isolated yield.

Received: March 20, 2012

Published: May 2, 2012

2.2. Hydrogenation Reactions. Reactions were performed on a 6 mmol substrate scale. Conversion was assessed by TLC analysis (hexane/ethyl acetate = 5:1 volume ratio) and by GC/MS analysis. The substrate was dissolved in 24 mL solvent for 0.25 M concentration and then treated with 0.1 mol % SiliaCat Pd⁰ sol–gel-entrapped catalyst (0.05 mmol g⁻¹ load). A 100 mL two-necked flask charged with the mixture was degassed two times, replacing each time the vacuum by hydrogen. The reaction mixture, connected to a balloon of hydrogen, was vigorously stirred at room temperature until GC/MS analysis showed maximum conversion. The catalyst was then filtered off and rinsed with THF, whereas the filtrate was concentrated to give a crude product. In the reusability test the hydrogenation was carried out under a hydrogen balloon at room temperature in the presence of 0.1 mol % sol–gel catalyst. A two-necked flask connected to a balloon of hydrogen was charged with substrate, solvent, and SiliaCat Pd⁰ and degassed two times, replacing each time the vacuum by hydrogen. The reaction mixture, connected to the balloon of hydrogen, was vigorously stirred at room temperature for 2 h after which the catalyst was recovered by filtration, rinsed with THF and dried under vacuum prior to reuse. The filtrate

was concentrated to give a crude product that was analyzed by ICP-OES for leaching of Pd and Si.

3. RESULTS AND DISCUSSION

3.1. Solvent Effect. To study the influence of the solvent on the catalytic process the SiliaCat Pd⁰ catalyst was first tested in hydrogenation of 1-decene to decane (entries 1–7 in Table 1) and of the less soluble 1-octadecene to octadecane (entries 8–15) over 0.1 mol % Pd catalyst. Different concentrations were first tested for 1-decene in methanol (entries 1–3 in Table 1) and best results were obtained for 0.25 M concentration with respect to the substrate (100% conversion after 0.5 h, entry 2). This concentration was used to test other solvents including ethanol, tetrahydrofuran, ethyl acetate, and hexane (entries 4–7), with the latter solvent showing the same excellent effect as methanol.

The substrate 1-octadecene is not soluble in methanol but is very soluble in THF and in MeOH/THF mixture. Hence, hydrogenation was carried out for different concentrations of the substrate in solvent, from 0.2 to 0.5 M, obtaining complete conversion in each case after 0.5 h (entries 8–14 in Table 1).

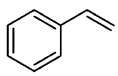
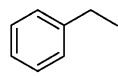
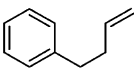
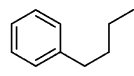
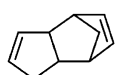
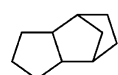
Table 2. Catalytic reactivity of SiliaCat Pd⁰ heterogeneous catalyst in reduction of 1-octadecene

entry	substrate	catalyst (mol %)	solvent (M)	time (h)	conv (yield) ^a (%)	TON	TOF/h
1 ^b	1-octadecene	0.1	MeOH/THF(1:1) (0.5 M)	0.5	100 (99)	990	1980
2 ^c	1-octadecene	0.02	MeOH/THF(1:1) (0.5 M)	3	98 (97.5)	4875	1625
3 ^d	1-octadecene	0.01	MeOH/THF(1:1) (0.5 M)	5	95 (94.2)	9420	1884
4 ^b	1-decene	0.1	MeOH (0.25M)	0.5	100	1000	2000
5 ^e	1-decene	0.02	MeOH (0.25M)	4	95	4750	1188
6 ^e	1-decene	0.01	MeOH (0.25M)	6	97	9700	1617

^aEvaluated by GC/MS analysis. Isolated yield. ^bExperimental conditions: 6 mmol substrate in 24 mL MeOH/THF (1:1 by volume ratio) and 0.1 mol % SiliaCat Pd⁰ catalyst. ^cExperimental conditions: 30 mmol substrate in 60 mL MeOH/THF (1:1 by volume ratio) and 0.02 mol % SiliaCat Pd⁰ catalyst.

^dExperimental conditions: 60 mmol substrate in 120 mL MeOH/THF (1:1 volume ratio) and 0.01 mol % SiliaCat Pd⁰ catalyst. ^eExperimental conditions: 71.5 mmol substrate in 285 mL MeOH and 0.02–0.01 mol % SiliaCat Pd⁰ catalyst under hydrogen balloon room temperature conditions.

Table 3. Catalytic hydrogenation of non-functionalised alkenes over SiliaCat Pd⁰ under mild conditions

Entry	Substrate	Catalyst (mol%)	Solvent (M)	Time (h)	Product	Conv.(Yield) ^b (%)	Select ^b (%)
1	1-Hexene	0.1	MeOH (0.25 M)	0.5	Hexane	100	-
2	1-Octene	0.1	MeOH (0.25 M)	0.5	Octane	100	99
3	1-Decene	0.1	MeOH (0.25 M)	0.5	Decane	100	99
4	1-Octadecene	0.1	MeOH/THF(4:1) (0.25 M)	0.5	Octadecane	100 (98.7)	99
5		0.1	MeOH (0.25 M)	0.5 1		94 100	100
6		0.1	MeOH (0.25 M)	1		100	99
7	Cyclohexene	0.1	MeOH (0.25 M)	1	Cyclohexane	100	99
8		0.1	MeOH (0.25 M)	1 2		80 100	100

^aExperimental conditions: 6 mmol substrate in 24 mL solvent (HPLC grade) and 0.1 mol % SiliaCat Pd⁰ catalyst, under hydrogen balloon room temperature conditions. ^bEvaluated by GC/MS analysis. Isolated yield.

Methanol has again a positive effect as reaction in THF only required 1 h to achieve full substrate hydrogenation (entry 15).

3.2. Catalyst Activity. Substrates 1-octadecene and 1-decene were used also to assess the catalytic activity of the sol-gel-entrapped catalyst. Hydrogenation of 1-octadecene over 0.1 mol % SiliaCat Pd⁰ proceeds with full conversion after 30 min (entry 1 in Table 2). Remarkably, with 0.02 mol % Pd catalyst the isolated yield was 97.5% after 3 h (entry 2) and for 0.01 mol % Pd catalyst the isolated yield was 94.2% after 5 h affording an impressive 9420 TON value (entry 3 in Table 2).

Hydrogenation of 1-decene over 0.1 mol % catalyst proceeded with full conversion after 30 min (entry 4), and with 95% conversion after 4 h over 0.02 mol % (entry 5). The employment of 0.01 mol % catalyst required 6 h to achieve 97% with a remarkable 9700 TON value (entry 6).

3.3. Scope of the Method. The scope of the method was investigated by carrying out the hydrogenation of a variety of olefins as well as of different olefins containing different functionalities. SiliaCat Pd⁰ was thus tested under hydrogen balloon room temperature conditions in methanol, ethanol, and THF over 0.1 mol % solid catalyst. Results in Tables 3 and 4 show that, in general, complete substrate conversion was obtained after 0.5–3 h, and typically after 1 h.

The optimised reaction conditions were first applied to a variety of nonfunctionalised olefins (Table 3). Terminal alkenes of widely different molecular size were easily reduced to the corresponding hydrogenated products in quantitative yield under remarkably mild conditions (entries 1–6 in Table 3). Cyclic substrates were also successfully converted into cycloalkanes (entries 7, 8).

3.4. Catalyst Selectivity. We next studied the reduction of a series of functionalised olefins (Table 4). The chemoselectivity toward two or more reducible functional groups in the catalytic hydrogenation is of great importance. Generally, the chemoselectivity is achieved by poisoning catalysts with ligands such as sulfur- or nitrogen-containing¹¹ molecules. However, this approach suffers from a disadvantage that large catalyst amount are used to compensate reduced catalytic activity. SiliaCat Pd⁰, on the other hand, displayed good selectivity retaining the high activity reported above for simpler alkenes. Selectivity (yield/conversion × 100) yield and conversion were also evaluated by GC/MS.

Hence, the same low (0.1 mol %) catalytic amount of SiliaCat Pd⁰ under the same mild H₂ balloon conditions was enough to mediate the selective hydrogenation of different alkenes bearing other reducible groups such as amine, halide, carbonyl, carboxyl, and esters (Table 4).

The hydrogenation of cinnamic acid was tested in methanol, ethanol, and in THF (entries 6–8 in Table 4). Whereas in methanol and in ethanol the formation of esters as methyl 3-phenylpropanoate and ethyl 3-phenylpropanoate was observed along with the hydrogenated acids (entries 6 and 7), complete selectivity is obtained in THF with full conversion of cinnamic acid to hydrocinnamic acid (100% conversion after 4 h, entry 8). For comparison, a modern 5% Pd/C commercial catalysts employed in this reaction affords a maximum 74% yield.¹²

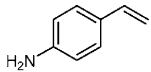
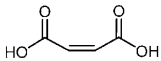
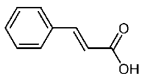
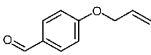
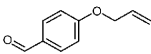
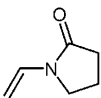
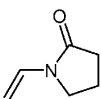
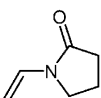
Hydrogenation of 4-(allyloxy)benzaldehyde to 4-propoxybenzaldehyde can be carried out in pure EtOH (entry 10 in Table 4) even if best results in terms of both activity and selectivity are obtained in THF (entry 11). On the other hand, catalytic hydrogenation of 5-hexen-2-one in EtOH (entry 12) is slightly faster than in THF (entry 13) with complete conversion after 2 h in both cases. Good results were obtained in each

Table 4. Catalytic hydrogenation of functionalised alkenes over SiliaCat Pd⁰ under mild conditions^a

Entry	Substrate	Catalyst (mol %)	Solvent (M)	Time (h)	Product	Conv(Yield) ^b (%)	Select ^b (%)
1		0.1	MeOH (0.25 M)	0.5		92 100 (99.1)	100
2		0.1	MeOH (0.25 M)	1		22 35	
3		0.25	MeOH (0.25 M)	1		100	99
4		0.5	MeOH (0.25 M)	0.5		100 (98.5)	100
5		0.1	MeOH (0.25 M)	1		100(98.9)	99.5
6 ^c		0.1	THF (0.25 M)	1		100(99.4)	100
7 ^c		0.1	MeOH (0.25 M)	4		100 100	95 20
8 ^c		0.1	EtOH (0.25 M)	1		90 100	100 75
9 ^c		0.1	THF (0.25 M)	2		100 100 (99.6)	100 100
10		0.1	MeOH (0.25 M)	0.5		100(99.5)	100
11		0.1	EtOH (0.25 M)	1		92 100	95
12		0.1	THF (0.25 M)	0.5		100 (96.4)	97
13		0.1	EtOH (0.25 M)	0.5		72 100	100
14		0.1	THF (0.25 M)	2		60 100	100
15		0.1	MeOH (0.25 M)	0.5		100(99.5)	100
16		0.1	EtOH (0.25 M)	0.5		100(99.6)	100
17		0.1	THF (0.25 M)	0.5		100	98
18		0.1	MeOH (0.25 M)	2	heptane	100	99
19 ^d		0.1	MeOH (0.25 M)	3	1-octadecane	100 100(97.3)	65 98
19 ^e		0.1	MeOH (0.25 M)	1		100	20
				2		100	100

^aExperimental conditions: 6 mmol substrate in 24 mL solvent (HPLC grade) and 0.1 mol % SiliaCat Pd⁰ catalyst, under hydrogen balloon room temperature conditions. ^bEvaluated by GC/MS analysis. Isolated yield. ^cAfter more than 1 h, the formation of methyl 3-phenylpropanoate was observed in methanol or ethyl 3-phenylpropanoate in ethanol. 100% selectivity was obtained in THF. ^dAfter 2 h, complete conversion of 1-octadecyne in 1-octadecene (35%) and octadecane (65%); after 3 h complete conversion in octadecane. ^eAfter 1 h, 100% conversion but 20% ethyl benzene and 80% styrene; after 2 h 100% ethyl benzene.

Table 5. Catalytic hydrogenation of different olefins with SiliaCat Pd⁰. leaching test

Entry	Substrate	Catalyst (mol%)	Solvent (M)	Time (h)	Conv. (Yield) ^a (%)	Leaching ^b (ppm)	
						Pd	Si
1 ^c	1-Octadecene	0.1	MeOH/THF(4:1) (0.25 M)	0.5	100 (98.7)	0.12 (2.3)	0.1 (1.9)
2 ^c	1-Octadecene	0.1	MeOH/THF(4:1) (0.5 M)	0.5	99 (98.7)	0.25 (4.9)	0.21 (4.1)
3 ^c	1-Octadecene	0.1	THF (0.5 M)	0.5	95	0.13 (2.6)	0.17 (3.4)
4 ^c	1-Octadecene	0.02	MeOH/THF(1:1) (0.5 M)	3	98 (97.5)	0.13 (2.5)	0.11 (2.2)
5 ^c	1-Octadecene	0.01	MeOH/THF(1:1) (0.5 M)	5	95 (94.2)	0.01 (0.2)	0.09 (1.9)
6		0.1	MeOH (0.25M)	0.5 1	92 100 (99.1)	0.3 (5.7)	1.3 (27.2)
7		0.1	MeOH (0.25M)	1 2	100(98.9)	0.04 (0.8)	0.05 (0.99)
8		0.1	THF (0.25M)	2	100(99.6)	0.05 (0.9)	0.05 (0.99)
9		0.1	EtOH (0.25M)	0.5 1	92 100	0.06 (1.2)	0.05 (0.99)
10		0.1	THF (0.25M)	0.5	100 (96.4)	0.13 (2.6)	0.12 (2.4)
11		0.1	MeOH (0.25M)	0.5	100(99.5)	0.26 (5.1)	0.44 (8.6)
12		0.1	EtOH (0.25M)	0.5	100(99.6)	0.42 (8.3)	0.1 (1.9)
13		0.1	THF (0.25M)	0.5	100 (99.2)	0.38 (7.4)	0.05 (0.99)
14 ^c	1-Octadecyne	0.1	MeOH (0.25M)	2 3	100 100(97.3)	0.25 (4.9)	0.25 (4.9)

^aConversion evaluated by GC/MS. Isolated yield. ^bLeaching of Pd and Si determined by ICP-OES analysis in DMF solution (50 mg/mL) and in solid crude product. ^cLeaching of Pd and Si determined by ICP-OES analysis in 1-pentanol solution (50 mg/mL) and in solid crude product.

case in the hydrogenation of 1-vinyl-2-pyrrolidone in MeOH, EtOH, and in THF (entries 14–16). Finally, SiliaCat Pd⁰ was also tested in the catalytic hydrogenation reaction of different alkynes such as 1-heptyne, 1-octadecyne, and phenyl acetylene (entries 17–19), obtaining total conversion into heptanes, octadecane, and ethyl benzene, respectively, after 2 or 3 h.

3.5. Metal Leaching and Catalyst Reusability. Possible leaching of Pd and Si from the SiliaCat Pd⁰ catalyst during conversion was analysed by ICP-OES in solid crude product and in solution for different conditions tested in the hydrogenation of 1-octadecene as well as of different olefins (Table 5). In general, values of leached Pd in isolated crude product are <5 ppm except for 4-aminostyrene (entry 5) and for 1-vinyl-2-pyrrolidinone (entries 11–13 in Table 5), pointing to some dissolution effect towards entrapped Pd(0) nanocrystals most likely due to coordination of the electron pair of the nitrogen atoms.

The reusability of SiliaCat Pd⁰ catalyst was explored in hydrogenation of *trans*-cinnamic acid (eq 1) under the optimal reaction conditions identified in Table 4.

Reusing the SiliaCat Pd⁰ catalyst in five consecutive cycles (Table 6) did not show any loss in catalytic activity with minimal leaching of Pd and Si (assessed by ICP-OES). Complete substrate conversion was obtained even after the fifth cycle, with 99% selectivity.

In summary, we have discovered that organosilica SiliaCat Pd(0) xerogel doped with nanostructured Pd(0) is a highly active, chemoselective, and readily reusable catalyst for the hydrogenation reaction of a large variety of olefins under remarkable mild conditions, namely hydrogen balloon at room temperature. Results are very interesting: high conversion and selectivity, even using mild conditions and very low (0.1 mol %) catalyst amount, were obtained for almost all the reactions studied in this work.

Table 6. Reusability of the SiliaCat Pd⁰ hydrogel in the selective catalytic hydrogenation of *trans*-cinnamic acid under mild conditions

run	time (h)	conversion (yield) ^a (%)	selectivity (%)	leaching ^b (ppm)	
				Pd	Si
1	2	100 (99.4)	100	0.09 (1.8)	0.06 (1.2)
2	2	100 (99.8)	100	0.09 (1.8)	0.03 (0.6)
3	2	100 (99.3)	100	0.12 (2.3)	0.02 (0.4)
4	2	100	99	0.09 (1.6)	0.03 (0.5)
5	2	100	99	0.08 (1.5)	0.02 (0.3)

^aConversion in final product determined by GC/MS analysis. Isolated yield of the crude product. ^bLeaching in Pd and Si determined by ICP-OES analysis in solution (DMF solvent 50 mg/mL, with respect to the crude product) and in the solid crude product.

The performance of the new catalyst is often superior to conventional solid Pd-based catalysts. For example, in the hydrogenation of cinnamic acid, the SiliaCat Pd(0) catalyst gave considerably higher yields in hydrocinnamic acid than a Pd(5%)/C commercial catalyst. Leaching of entrapped Pd is negligible. We ascribe the excellent performance of the SiliaCat Pd(0) material to both the ultrasmall (2–4 nm) size of the crystalline Pd nanoparticles as well as to their sol–gel entrapment in the organosilica matrix. The former aspect is crucial and has been discussed in detail by us in a recent structural characterization study of the SiliaCat Pd(0) material.¹³ Entrapment within the methylated silica cages, in its turn, imparts physical and chemical stabilization to the entrapped nanoparticles while ensuring optimal diffusion of the reactants through the huge (600–800 m²/g) inner porosity of the organically modified silicate (ORMOSIL). Again, the relevance of the latter aspect in the catalytic performance of doped ORMOSIL has been studied and explained elsewhere.¹⁴

In conclusion, given the low amount of Pd catalyst required and the easy scalability of batch processes employing ORMOSIL catalysts,¹⁵ the route may be open to widespread employment of catalytic hydrogenation for alkenes reduction both in industry and in the laboratory.

AUTHOR INFORMATION

Corresponding Author

fbeland@silicycle.com (F.B.); mario.pagliaro@cnr.it (M.P.)

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This paper is dedicated with affection to Montpellier's ENCSM Professor Joël Moreau for his eminent contributions to the progress of chemical catalysis through sol–gel materials.

REFERENCES

- (1) Cui, X.; Burgess, K. *Chem. Rev.* **2005**, *105*, 3272–3296.
- (2) Nishimura, S. *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*; John Wiley & Sons: New York, NY, 2001.
- (3) Pasto, D. J. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 8, Chapter 3.3.
- (4) Rangheard, C.; de Julián Fernández, C.; Phua, P.-H.; Hoorn, J.; Lefort, L.; de Vries, J. G. *Dalton Trans.* **2010**, *39*, 8464–8471.
- (5) Koutsopoulos, S.; Johannessen, T.; Eriksen, K. M.; Fehrmann, R. *J. Catal.* **2006**, *238*, 206–213.
- (6) Chung, M.-K.; Schlaf, M. *J. Am. Chem. Soc.* **2004**, *126*, 7386–7392.

(7) Hagio, H.; Sugiura, M.; Kobayashi, S. *Org. Lett.* **2006**, *8*, 375–378.

(8) Pagliaro, M.; Pandarus, V.; Ciriminna, R.; Béland, F.; Carà, P. D. *ChemCatChem* **2012**, *4*, 432–445.

(9) Pandarus, V.; Ciriminna, R.; Béland, F.; Pagliaro, M. *Catal. Sci. Technol.* **2011**, *1*, 1616–1623.

(10) Park, C. M.; Kwon, M. S.; Park, J. *Synthesis* **2006**, 3790–3794.

(11) (a) Ikawa, T.; Sajiki, H.; Hirota, K. *Tetrahedron* **2005**, *61*, 2217–2231. (b) Mori, A.; Mizusaki, T.; Miyakawa, Y.; Ohashi, E.; Haga, T.; Maegawa, T.; Monguchi, Y.; Sajiki, H. *Tetrahedron* **2006**, *62*, 11925–11932.

(12) Morrow, J.; Carson, J.; Arunajatesan, V. Catalyst Design for the Hydrogenation of Cinnamic Acid to Hydrocinnamic Acid. In *Proceedings of the 21st North American Catalysis Society Meeting 2009*; Curran Associates, Inc.: Red Hook, NY, 2011; Vol. 1, p 897.

(13) Pandarus, V.; Béland, F.; Ciriminna, R.; Demma Carà, P.; Pagliaro, M. *Catal. Lett.* **2012**, *142*, 213–217.

(14) Fidalgo, A.; Ciriminna, R.; Ilharco, L. M.; Pagliaro, M. *Chem. Mater.* **2005**, *17*, 6686–6694.

(15) For details, see the URL: www.silicycle.com/products/siliacat-heterogeneous-catalysts.