doi:10.1246/cl.2011.405

Highly Efficient Pd/SiO_2–Dimethyl Sulfoxide Catalyst System for Selective Semihydrogenation of Alkynes

Yusuke Takahashi,[1] Norifumi Hashimoto,[1] Takayoshi Hara,[2] Shogo Shimazu,[2] Takato Mitsudome,[1]
Tomoo Mizugaki,[1] Koichiro Jitsukawa,[1] and Kiyotomi Kaneda*[1,3]
[1]*Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531*
[2]*Graduate School of Engineering, Chiba University, 1-33 Yayoi, Inage-ku, Chiba 263-8522*
[3]*Research Center for Solar Energy Chemistry, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531*

(Received January 27, 2011; CL-110066; E-mail: kaneda@cheng.es.osaka-u.ac.jp)

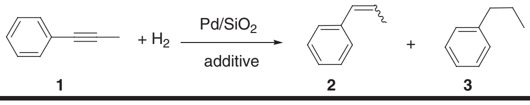
Silica-supported Pd nanoparticles (Pd/SiO_2) with dimethyl sulfoxide (DMSO) show excellent catalytic activity and selectivity for the semihydrogenation of alkynes. Small amounts of DMSO drastically suppress the overhydrogenation and isomerization of alkenes. This catalyst system is also applicable to both internal and terminal alkynes. Furthermore, the Pd/SiO_2 catalyst was separable from the reaction mixture after the hydrogenation and reusable without loss of its high catalytic activity or selectivity.

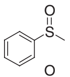
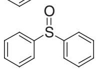
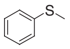
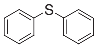
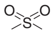
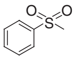
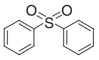
The selective hydrogenation of alkynes to (*Z*)-alkenes is of great importance for the construction of a variety of valuable compounds such as bioactive molecules, natural products, and industrial materials.[1] Lindlar catalyst has been widely employed for a long time for this purpose.[2] However, Lindlar catalyst must be pretreated with environmentally harmful Pb compounds during the preparation of the catalyst and also requires considerable amounts of quinoline as an additive to achieve the selective semihydrogenation. Moreover, Lindlar catalyst suffers from substrate limitations in that only internal alkynes are selectively hydrogenated into the desired alkenes whereas terminal alkynes are generally overhydrogenated into alkanes.[3] From the perspective of green chemistry and other practical concerns, the development of more environmentally benign and efficient catalyst systems for the semihydrogenation of alkynes is highly desired. There have been some successful catalytic methods for the semihydrogenation of alkynes using H_2.[4–9] For example, Sajiki and co-workers have developed a polyethyleneimine-supported Pd catalyst that promoted highly selective hydrogenation of a wide range of alkynes to alkenes without any additives.[7] Ohkuma and co-workers also have reported an efficient catalytic system using colloidal Pd nanoparticle–tetrabutylammonium borohydride that showed good turnover frequency (5000 min^{-1}) under a pressurized atmosphere of H_2.[8]

Herein, we report that silica-supported Pd nanoparticles (Pd/SiO_2) with dimethyl sulfoxide (DMSO) show excellent catalytic activity and selectivity for the semihydrogenation of alkynes. Small amounts of DMSO drastically suppress the overhydrogenation and isomerization of alkenes.[10] This catalyst system is also applicable to terminal alkynes as well as internal ones.

The SiO_2-supported Pd catalyst was synthesized as follows. Silica (CARiACT Q-30:FUJI Silysia Chemical, Ltd.) was added to an aqueous solution of $[Pd(NH_3)_4Cl_2]\cdot H_2O$ (1.0 mM), and then the mixture was stirred for 12 h in air at 30 °C. The resulting slurry was filtered, washed with deionized water, and dried in vacuo at room temperature to yield a silica-supported Pd^{II} species as a white powder. Next, the obtained solid was treated with ethanol at 85 °C for 2 h under an argon atmosphere to give Pd/SiO_2 as a grayish-brown powder. The loading amount of Pd in Pd/SiO_2 was determined by elemental analysis to be 0.046 mmol g^{-1}. The TEM image of Pd/SiO_2 revealed that Pd nanoparticles were formed on SiO_2 whose mean diameter was estimated as 5.3 nm.[11]

Table 1. Hydrogenation of 1-phenyl-1-propyne catalyzed by Pd/SiO_2 in the presence of various sulfur compounds[a]



Entry	Additive	Time /min	Conv. /%[b]	Sel. of **2** /%[b]	*Z*:*E*
1		90	100	98	98:2
2		90	100	96	98:2
3		90	100	95	98:2
4		80	100	92	98:2
5		90	100	95	98:2
6		70	100	95	98:2
7[c]		15	100	72	95:5
8[c]		15	100	75	93:7
9[c]		15	100	70	96:4
10	No	15	100	72	95:5

[a]Reaction conditions: Pd/SiO_2 (0.010 g, Pd; 0.46 µmol), 1-phenyl-1-propyne (0.5 mmol), additive (10 µmol), *n*-hexane (5 mL), 30 °C, H_2 (1 atm). [b]Determined by GC using an internal standard. [c]In THF.

The hydrogenation of 1-phenyl-1-propyne (**1**) was carried out using Pd/SiO_2 under 1 atm of H_2 at 30 °C in the presence of various sulfur compounds such as sulfides, sulfoxides, and sulfones.[12] The results are summarized in Table 1. Among the sulfur compounds tested, sulfoxides and sulfides were found to be effective additives (Entries 1–6) to afford 1-phenyl-1-propene (**2**) in >92% yields. DMSO provided the best efficiency in the semihydrogenation of **1**, giving **2** in 98% yield with 98% (*Z*)-selectivity. In contrast, the addition of sulfones improved neither the yield nor the selectivity of **2** (Entries 7–9 vs. 10).

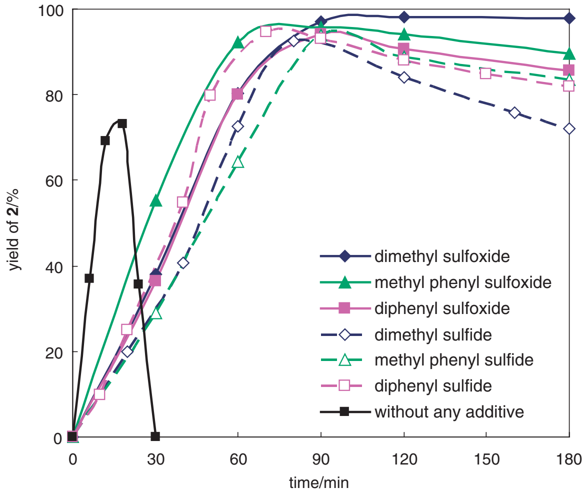
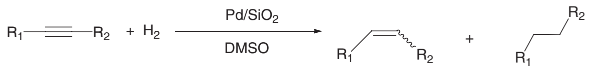


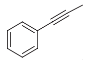
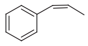
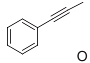
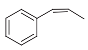
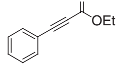
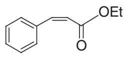
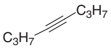
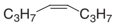
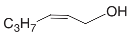
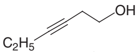
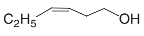
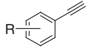
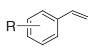
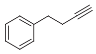
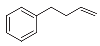
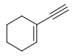
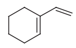
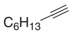
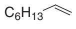
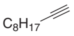
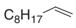
Figure 1. Time course for hydrogenation of 1-phenyl-1-propyne catalyzed by Pd/SiO_2 with sulfoxides or sulfides. Reaction conditions: Pd/SiO_2 (0.010 g, Pd; 0.46 µmol), **1** (0.5 mmol), DMSO (10 µmol), *n*-hexane (5 mL), 30 °C, H_2 (1 atm).

Figure 1 shows time courses for the above hydrogenation of **1** using Pd/SiO_2 with sulfoxides or sulfides. The addition of small amounts (2 mol %) of sulfoxides and sulfides significantly suppressed the hydrogenation of **2** after the complete conversion of **1**, whereas the hydrogenation of **2** to *n*-propylbenzene (**3**) rapidly proceeded in the absence of sulfur compounds. In the case of DMSO, the hydrogenation of **2** hardly occurred and the high selectivity of **2** was maintained even after full conversion of **1**. This result clearly illustrates that DMSO is the most effective additive for the semihydrogenation of **1**. The reaction mixture was filtered at 50% conversion of **1**. Continuous stirring of the filtrate under 1 atm of H_2 did not yield any further products, indicating that the hydrogenation took place at the Pd NPs on the surface of SiO_2.

The scope of substrates was investigated using the optimized set of Pd/SiO_2 with DMSO. As summarized in Table 2, various internal alkynes were selectively converted into the corresponding (*Z*)-alkenes with high yields (Entries 1–6). It is known that the semihydrogenation of terminal alkynes is difficult using Lindlar catalyst.[3] Interestingly, the present Pd/SiO_2–DMSO catalyst system is extensively applicable to the highly selective semihydrogenation of terminal alkynes. For example, a series of phenylacetylenes having electron-withdrawing or -donating groups were selectively hydrogenated into the corresponding styrene derivatives (Entries 7–12). In addition, reducible bromo and nitro groups remained intact during the hydrogenations (Entries 11 and 12). Other terminal aliphatic alkynes also afforded the corresponding alkenes in excellent yields (Entries 13–16). The isolation of the products from the present catalyst system was easy. After the semihydrogenation was completed, Pd/SiO_2 was separated from the reaction mixture by simple filtration. Next, the solvent was evaporated, and then the residue was purified by silica gel chromatography, providing the pure alkenes. The spent Pd/SiO_2 catalyst was reusable and maintained high catalytic performance in the presence of small amounts of DMSO (Entry 2). Furthermore, the Pd/SiO_2–DMSO catalyst system worked well even under preparative scale reaction conditions. Namely, 1.16 g (10 mmol) of **1** was converted selectively to provide 1.09 g of **2** (94% isolated yield, $Z/E = 98/2$).[11]

Table 2. Semihydrogenation of various alkynes to alkenes using Pd/SiO_2–DMSO catalyst system[a]



Entry	Substrate	Product	Time /min	Yield of alkene /%[b]	Z:E
1			90	98	98:2
2[c]			90	98	98:2
3[d]			180	98	92:8
4[d,e]			360	99	97:3
5[d]			210	99	99:1
6[d]			150	97	99:1
7[f]	 R = H	 R = H	60	98	—
8[f]	R = 4-Me	R = 4-Me	60	98	—
9[f]	R = 4-MeO	R = 4-MeO	300	98	—
10[f]	R = 4-NH_2	R = 4-NH_2	120	98	—
11[f]	R = 4-Br	R = 4-Br	180	98	—
12[f]	R = 2-NO_2	R = 2-NO_2	180	98	—
13[f]			60	98	—
14[f]			120	98	—
15[f]			60	98	—
16[f]			30	98	—

[a]Reaction conditions: Pd/SiO_2 (Pd: 0.46 µmol), substrate (0.5 mmol), DMSO (10 µmol), *n*-hexane (5 mL), 30 °C, H_2 (1 atm). [b]Determined by GC using an internal standard technique. [c]Reuse. [d]40 °C. [e]Isomerized product 3-octene was not formed at all. [f]DMSO (0.2 mmol).

To investigate the role of DMSO in the selective semihydrogenation of alkynes, an adsorption study was conducted. Into a glass reactor, phenylacetylene, styrene, and Pd/SiO_2 were added to *n*-hexane in the presence or absence of DMSO, and the mixture was stirred at room temperature for 1 h. Gas chromatographic analysis of the filtrate revealed that both phenylacetylene and styrene were adsorbed on Pd/SiO_2 in the absence of DMSO. On the other hand, when DMSO was added, styrene was not adsorbed at all whereas phenylacetylene was adsorbed.[11] This phenomenon suggests that the preferential adsorption of DMSO to alkene products for the Pd/SiO_2 catalyst suppresses the overhydrogenation of the alkenes. The results are in agreement with the observation that product **2** shows extremely low reactivity after complete conversion of **1** in the presence of DMSO (see above).

In conclusion, the catalytic system of Pd/SiO_2 with DMSO had excellent activity and selectivity for the semihydrogenation of various terminal alkynes as well as internal alkynes. Moreover, this catalyst system was reusable and applicable to a preparative scale reaction. It was found that the suitable adsorption ability of DMSO for the Pd nanoparticles led to the highly selective semihydrogenation of alkynes.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References and Notes

1 a) E. N. Marvell, T. Li, *Synthesis* **1973**, 457. b) R. L. Burwell, Jr., *Chem. Rev.* **1957**, *57*, 895.
2 H. Lindlar, *Helv. Chim. Acta* **1952**, *35*, 446.
3 H. Lindlar, R. Dubuis, *Org. Synth. Coll. Vol.* **1973**, *5*, 880.
4 N. M. Yoon, K. B. Park, H. J. Lee, J. Choi, *Tetrahedron Lett.* **1996**, *37*, 8527.
5 M. W. van Laren, C. J. Elsevier, *Angew. Chem., Int. Ed.* **1999**, *38*, 3715.
6 M. Gruttadauria, L. F. Liotta, R. Noto, G. Deganello, *Tetrahedron Lett.* **2001**, *42*, 2015.
7 a) H. Sajiki, S. Mori, T. Ohkubo, T. Ikawa, A. Kume, T. Maegawa, Y. Monguchi, *Chem.—Eur. J.* **2008**, *14*, 5109. b) S. Mori, T. Ohkubo, T. Ikawa, A. Kume, T. Maegawa, Y. Monguchi, H. Sajiki, *J. Mol. Catal. A: Chem.* **2009**, *307*, 77.
8 J. Hori, K. Murata, T. Sugai, H. Shinohara, R. Noyori, N. Arai, N. Kurono, T. Ohkuma, *Adv. Synth. Catal.* **2009**, *351*, 3143.
9 T. Mizugaki, M. Murata, S. Fukubayashi, T. Mitsudome, K. Jitsukawa, K. Kaneda, *Chem. Commun.* **2008**, 241.
10 We have found that supported Pd catalysts with dimethyl sulfoxide (DMSO) as a solvent gave selective semihydrogenation of alkynes, see: a) M. Terasawa, H. Yamamoto, K. Kaneda, T. Imanaka, S. Teranishi, *J. Catal.* **1979**, *57*, 315. b) S. Shimazu, W. Teramoto, T. Iba, M. Miura, T. Uematsu, *Catal. Today* **1989**, *6*, 141.
11 See Supporting Information[13] for details.
12 Quinoline, which is known as an effective additive in the Lindlar catalyst system, slightly improved the selectivity for **2** (conv. = 100%, sel. = 85%, $Z/E = 96/4$) under similar reaction conditions.
13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.