



## Highly efficient solvent-free catalytic hydrogenation of solid alkenes and nitro-aromatics using Pd nanoparticles entrapped in aluminum oxy-hydroxide

Fei Chang<sup>a</sup>, Hakwon Kim<sup>b,\*</sup>, Byeongno Lee<sup>b</sup>, Sungho Park<sup>c</sup>, Jaiwook Park<sup>c</sup>

<sup>a</sup>The School of Environment and Architecture, University of Shanghai for Science and Technology, Shanghai 200093, PR China

<sup>b</sup>Department of Applied Chemistry, Kyung Hee University, Gyeonggi-do 446-701, Republic of Korea

<sup>c</sup>Department of Chemistry, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea

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### ABSTRACT

Solid alkenes and aromatic nitro compounds are readily hydrogenated to the corresponding alkanes without further reduction of other functional group and amino compounds in nearly quantitative yields in the presence of Pd nanoparticles entrapped in aluminum oxy-hydroxide under the solvent-free condition.

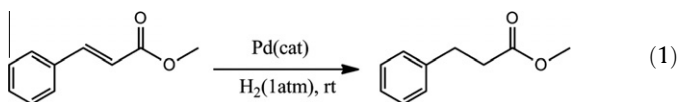
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Hydrogenation of alkenes and nitro-aromatics is synthetically important in organic transformation,<sup>1</sup> which provides alkanes and aromatic amines, widely utilized as intermediates for dyes, photographic materials, pharmaceutical chemicals, and antioxidants, respectively. However, conventional reduction procedures require organic solvents and work-up process that could cause environmental pollution. Therefore, many environmentally benign chemical processes have been developed to eliminate organic solvents from synthesis.<sup>2</sup> Solvent-free (solventless) reactions have attracted much attention because of the several advantages they have over traditional reactions in organic solvents: smaller reaction vessels, no organic medium, higher efficiency, easier operation, simpler purification, and different product distribution.<sup>3</sup> Palladium(0) catalysts are popular and important for many hydrogenation reactions of organic compounds.<sup>4</sup> In general, commercial Pd sources, such as Pd/C and Pd/Al<sub>2</sub>O<sub>3</sub>, show unsatisfactory results in selectivity and/or yield from the hydrogenation reactions that require high selectivity and low structure sensitivity probably due to Pd particles of variable size unevenly distributed upon the support surfaces.<sup>5</sup>

Hence, Pd nanoparticles have been investigated to improve selectivity and/or reactivity in organic reactions, especially hydrogenation.<sup>4</sup> Recently, Pd nanoparticles embedded in aluminum oxy-hydroxide, [Pd/AlO(OH)], as a robust and recyclable catalyst, were reported as a powerful catalyst to catalyze hydrogenation in organic mediums.<sup>6</sup> Herein, we report the catalytic hydrogenation of solid alkenes and aromatic nitro compounds using Pd/AlO(OH) under the solvent-free conditions at room temperature to give the corre-

sponding alkanes and amines in high selectivities and reactivities, respectively, which may afford an effective and environmentally benign methodology.

A preliminary study on the catalytic utility of Pd/AlO(OH) for solid substrates in the hydrogenation of methyl-cinnamate was performed with and without solvents.<sup>7</sup> Solvent-free hydrogenation of methyl-cinnamate was also examined with some commercially available Pd catalysts. Table 1 shows the results of the hydrogenation of solid methyl-cinnamate to methyl 3-phenylpropionate under various conditions. It is seen that a solid mixture of substrate and Pd/AlO(OH) catalyst (2 mol % of Pd) under atmospheric pressure of hydrogen at room temperature reacted within 5 s to give the saturated product in a satisfactory yield (entry 1). When the reaction time was extended to 30 s, an almost quantitative yield was observed (entries 2 and 3). Furthermore, quantitative conversions were still retained in the presence of smaller amounts (0.5 mol %) of Pd with a longer reaction time (10 min). Interestingly, solvent-free hydrogenations by commercially available Pd catalysts, such as Pd/C, Pd/Al<sub>2</sub>O<sub>3</sub>, and Pd/CaCO<sub>3</sub>, in even longer reaction time (60 s) did not afford the corresponding product in good yields (16%, 15%, and 4%, respectively, entries 4–6). We attributed this inefficiency to the bulky size and poor dispersion of Pd particles on the support.<sup>5</sup>



Pd/AlO(OH)-catalyzed hydrogenations of methyl-cinnamate in various organic solvents, such as methanol, acetone, tetrahydrofuran (THF), and hexane, were also examined and showed much lower efficiencies than those in solvent-free reactions (entries 7–10).

\* Corresponding author. Tel.: +82 31 201 2459; fax: +82 31 202 7337.  
E-mail address: [hwkim@khu.ac.kr](mailto:hwkim@khu.ac.kr) (H. Kim).

**Table 1**  
Hydrogenation of methyl-cinnamate using Pd catalysts under various conditions<sup>a</sup>

Entry	Catalysts	Solvents	Time (s)	Yield <sup>b</sup> (%)
1	Pd/AlO(OH)	No	5	81
2	Pd/AlO(OH)	No	10	90
3	Pd/AlO(OH)	No	30	99
4	Pd/C	No	60	16
5	Pd/Al <sub>2</sub> O <sub>3</sub>	No	60	15
6	Pd/CaCO <sub>3</sub>	No	60	4
7	Pd/AlO(OH)	Methanol	60	3
8	Pd/AlO(OH)	Acetone	60	6
9	Pd/AlO(OH)	THF	60	5
10	Pd/AlO(OH)	Hexane	60	2

<sup>a</sup> All reactions were performed at room temperature under atmospheric pressure of hydrogen gas. Methyl-cinnamate (0.20 mmol) was hydrogenated by the Pd catalyst (2 mol % of Pd) indicated in the table.

<sup>b</sup> Determined by GC analysis.

The rapid solvent-free hydrogenation observed can be rationalized with a higher concentration of the substrate under the solvent-free condition compared to that in organic solvent.<sup>8</sup>

Various solid alkenes containing the other functional group were conducted for this solvent-free reaction in the presence of Pd/AlO(OH) with hydrogen in order to confirm the reactivity and the chemoselectivity. The results are summarized in Table 2 (entries 1–9). Only double bond moiety of substrates was hydrogenated quantitatively using Pd/Al(O)OH catalyst in the absence of solvent without any further hydrogenation of the carbonyl, sulfonyl, or nitrile group. Most substrates were hydrogenated within 5 min. However, *trans*-stilbene (entry 8) and maleic acid (entry 9) showed lower reactivities under the same conditions: their corresponding products, bibenzyl and succinic acid, were obtained in only 89% and 82% yields, even after 2 h. According to the literature, it can be proposed that there is a close relationship between the yields obtained and the melting points of the substrates involved in the solvent-free hydrogenation.<sup>9</sup>

To extend the scope of the solvent-free hydrogenation, a series of solid aromatic nitro compounds containing diverse functional groups have been treated with Pd/AlO(OH). As shown in Table 2 (entries 10–14), all nitro substrates underwent nearly complete conversions to their corresponding aromatic amines in a short time.

To the best of our knowledge, this is the first Letter of a solvent-free hydrogenation of solid nitro-aromatics, though the solvent-free hydrogenation of liquid nitro compounds has been reported.<sup>10</sup> Although we did not obtain valuable microscopic evidence for the reaction mechanism, we observed macroscopically that the color of the solid mixture was changed quickly as the hydrogen gas was introduced into the reactor. Subsequently we did a comparative experiment using a simple mixture of blocky-shaped substrate and catalyst with and without grounding. It was observed that the blocky substrate melted immediately after introducing hydrogen gas. Also, as shown in Table 2, it was found that the efficiencies of solvent-free hydrogenations of solid substrates by Pd/AlO(OH) catalyst were closely depended on the melting points of the reactants. It seems that our solvent-free hydrogenations proceeded in a fused state based on this observation and the literature explanation,<sup>9,11</sup> although we may not exclude the possibility of the hydrogenation in the solid-to-solid state. Accordingly, we can suggest that substrates with low melting points can be easily melted into the fused state by the heat liberated from the exothermic hydrogenation, which can enhance the molecular mobility and the catalyst-substrate collisions to result in fast reaction. From this point of view, we may conclude that substrates with low melting points proceed very quickly for the solvent-free hydrogenation by Pd/AlO(OH) catalyst, and substrates with high melting points are

**Table 2**  
Hydrogenation of various solid alkenes and aromatic nitro compounds<sup>a</sup>

Entry	Substrate (mp, °C)	Product (mp, °C)	Time (min)	Yield <sup>b</sup> (%)
1	(30–33)	(-18)	1	98
2	(70–72)	(-6–3)	1	99
3	(65–70)	(-29)	3	95
4	(53)	(118–120)	1	99
5	(67–69)	(35–40)	2	99
6	(93–95)	(50–54)	5	96
7	(102–106)	(16–19)	5	99
8	(123–125)	(50–53)	120	89
9	(137–140)	(184–186)	120	82
10	(31–35)	(30–32)	5	99
11	(70–73)	(100–102)	5	99 <sup>c</sup>
12	(76–78)	(95–98)	5	95
13	(103–107)	(130–132)	30	92
14	(110–115)	(185–189)	10	99

<sup>a</sup> Without otherwise stated, substrate (0.2 mmol) was used in every entry with Pd/AlO(OH) (2 mol % of Pd) under atmospheric pressure of hydrogen gas at room temperature, without controlling the vessel temperature during the reaction.

<sup>b</sup> Determined by GC analysis.

<sup>c</sup> Determined by <sup>1</sup>H NMR analysis.

hydrogenated slowly under the same conditions. We also found that the aluminum oxy-hydroxide matrix in the Pd catalyst would be crucial for the remarkable catalytic activities in the solvent-free conditions.<sup>6a</sup> Also, it should be mentioned that the carbonyl group in the nitro-aromatic compound (entry 12) was not hydrogenated at all. Additionally, recyclability of Pd/AlO(OH) catalyst after the solvent-free reaction was examined in the hydrogenation of methyl-cinnamate and 2-fluoro-4-nitrotoluene. Methylene chloride or acetone was employed in order to recover Pd/AlO(OH) after

**Table 3**  
Reusability of Pd/AIO(OH)

Recovery	1st	2nd	3rd
Methyl-cinnamate	>99	>99	>99
2-Fluoro-4-nitrotoluene	>99	>99	95

solvent-free hydrogenation by simply washing and drying under vacuum. The Pd catalyst did not show any significant decrement of hydrogenation activity at least three times (see Table 3). Now we are trying to improve the recycling of the Pd catalyst using supercritical CO<sub>2</sub> extraction. More detailed results will be published in the near future.

In summary, we developed a highly efficient and selective solvent-free hydrogenation of solid alkenes and nitro-aromatic compounds using Pd/AIO(OH) to yield the corresponding alkanes and aromatic amines.

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### References and notes

- Larock, R. C., 2nd ed.; In *Comprehensive Organic Transformations*; Wiley-VCH: New York, 1999; Vol. 41. pp 7–11.
- Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025.
- (a) Cave, G. W. V.; Raston, C. L.; Scott, J. L. *Chem. Commun.* **2001**, 2159; (b) Hermans, S.; Raja, R.; Thomas, J. M.; Johnson, B. F. G.; Sankar, G.; Gleeson, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 1211.
- Tsuji, J. *Palladium Reagents and Catalysts: New Perspectives for the 21st Century*; John Wiley & Sons: Chichester, 2004.
- Lee, S.-S.; Park, B.-K.; Byeon, S.-H.; Chang, F.; Kim, H. *Chem. Mater.* **2006**, *18*, 5631.
- (a) Kwon, M. S.; Kim, N.; Park, C. M.; Lee, J. S.; Kang, K. Y.; Park, J. *Org. Lett.* **2005**, *7*, 1077; (b) Kwon, M. S.; Kim, N.; Seo, S. H.; Park, I. S.; Cheedra, R. K.; Park, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6913; (c) Choi, Y. K.; Kim, Y.; Han, K.; Park, J.; Kim, M.-J. *J. Org. Chem.* **2009**, *74*, 9543.
- All reactions were carried out in small and dried glassware (10 mL). Hydrogenation of methyl-cinnamate under solvent-free condition: a mixture of substrate and Pd/AIO(OH) (2.0 mol % of Pd) was ground finely with a mortar and pestle at room temperature before use, and then 0.081 g of the mixture (including 0.2 mmol methyl-cinnamate and a corresponding amount of catalyst) was loaded into a glassware equipped with a rubber septum, followed by sealing with parafilm. N<sub>2</sub> gas was charged into the reactor for several times to remove air and then was expelled by an atmosphere of hydrogen (0.1 Mpa). The mixture was then allowed to stand for a desired time without controlling the temperature in the vessel. After filtering the catalyst, the product analyses were performed using GC and <sup>1</sup>H NMR by comparing to the authentic samples. Hydrogenation of methyl-cinnamate in organic solvents: a mixture (0.081 g) of methyl-cinnamate and Pd/AIO(OH) in 1 mL organic solvent was hydrogenated at room temperature in a hydrogen atmosphere. After reaction, the analysis procedure was the same as described above.
- (a) Rothenberg, G.; Downie, A. P.; Raston, C. L.; Scott, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 8701; (b) Toda, F.; Yagi, M.; Kiyoshige, K. *Chem. Commun.* **1988**, 958.
- Nozoe, T.; Tanimoto, K.; Takemitsu, T.; Kitamura, T.; Harada, T.; Osawa, T.; Takayasu, O. *Solid State Ionics* **2001**, *141*, 695.
- Vass, A.; Dudas, J.; Toth, J.; Varma, R. S. *Tetrahedron Lett.* **2001**, *42*, 5347.
- Kitamura, T.; Harada, T. *Green Chem.* **2001**, *3*, 252.