Development of Silicon Carbide-Supported Palladium Catalysts and Their Application as Semihydrogenation Catalysts for Alkynes under Batch- and Continuous-Flow Conditions

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Abstract: Silicon carbide (SiC)-supported palladium (Pd) catalysts [3% Pd/SiC and a 3% Pd-diethylenetriamine (DETA)/SiC complex] for chemoselective hydrogenation under batch- and continuous-flow conditions were developed. The alkyne, alkene, azide, nitro, and benzylloxycarbonyl-protected aromatic amine (N-Cbz) functionalities were chemoselectively reduced in the presence of 3% Pd/SiC. By contrast, benzyl ether, alkyl N-Cbz, epoxide, aromatic chloride, aromatic ketone, and tert-butyl(dimethyl)silyl ether were tolerant to the 3% Pd/SiC-catalyzed hydrogenation. The combined use of 3% Pd/SiC and DETA demonstrated excellent chemoselectivity toward the semihydrogenation of various mono- and disubstituted alkynes under batch- and continuous-flow conditions. Furthermore, compared with the separate use of 3% Pd/SiC and DETA, the newly developed 3% Pd(DETA)/SiC-packed in a cartridge showed higher chemoselectivity toward the continuous-flow semihydrogenation of alkyne over 24 h.

Keywords: semihydrogenation; heterogeneous catalysis; alkynes; palladium; silicon carbide

1. Introduction

The semihydrogenation of alkynes to (Z)-alkenes is an essential transformation reaction for constructing the partial structures of bioactive or industrially valuable functional materials [1,2]. The Lindlar catalyst is a well-known semihydrogenation catalyst for carbon–carbon triple bonds. However, this catalyst must be pre-treated with lead(II) acetate [Pb(OAc)\textsubscript{2}] and added with quinoline as a catalyst poison to control the reaction [3,4]. Furthermore, the Lindlar catalyst is only applicable to the partial hydrogenation of disubstituted (internal) alkynes because the hydrogenation of monosubstituted alkynes proceeds efficiently to give alkanes as over-hydrogenated products. Various catalytic semihydrogenation reactions for alkynes have been reported using H\textsubscript{2} gas [5–10], hydrosilane [11], sodium borohydride [12], alcohol [13–16], formic acid [17,18], ammonium formate [19], amine [20], ammonia borane [21,22], water [23–25], and so on [26,27]. Heterogeneously catalyzed semihydrogenation reactions using H\textsubscript{2} gas, a clean and inexpensive hydrogen source under ambient temperature and atmospheric pressure, are generally desired owing to their cost efficiency, ease of handling, and potential for development into an environmentally friendly method. Several heterogeneous metal catalysts for semihydrogenation, such as Pd nanoparticles stabilized by an anionic surfactant [28] or caged in metal-organic frameworks [29], Cu nanoparticles with specific ligands [30,31], Pd-Cu on TiO\textsubscript{2} photocatalysts [32], in situ prepared Fe nanoparticles [33], size- and structure-
defined Pd or Cu nanoparticles [34–36], Pt plates for electrocatalyzed semihydrogenation [37], and highly chemoselective bi- or trimetallic catalysts [38–45], and so on [26,27,46–49], have been developed. The intentional use of the catalyst-poisoning effect induced by co-ordinating amines [50–64] or sulfides [65–69] as an additive or catalyst support is a practical approach to achieve chemoselective hydrogenation [70,71]. We previously developed heterogeneous catalysts (Pd/PEI [50,51] and Pd/BN [52,53]) for the semihydrogenation of alkenes.

Herein, we report the development of a heterogeneous Pd catalyst (Pd/SiC) supported on SiC for chemoselective hydrogenation. SiC is a robust, refractory, and chemically stable material. We focused on the physical and chemical stability of the catalyst support for chemoselective hydrogenation [72]. We also prepared a Pd-diethylenetriamine (DETA)/SiC complex for the semihydrogenation of mono- and disubstituted alkenes under ordinary H2 pressure and ambient temperature. Pd(DETA)/SiC can be used under batch and continuous-flow conditions.

2. Results

The catalytic activity of 3% Pd/SiC for hydrogenation was evaluated at 25 °C under H2 in MeOH (Table 1). The alkyne (1a, Entry 1), nitro (4, Entry 2), and azide (6, Entry 3) functionalities were smoothly hydrogenated. The aromatic N-benzyloxy carbonyl (Cbz) group (7) underwent hydrogenolysis at 50 °C to afford the corresponding aniline derivative (8). By contrast, the aliphatic N-Cbz protecting group (9) was tolerant to the 3% Pd/SiC-catalyzed hydrogenation conditions (Entries 4 vs. 5). 2,2-Dimethylpropionophenone (10, Entry 6) and benzyl benzoate (11, Entry 7) were hardly hydrogenated, even after 24 h of reaction in EtOAc instead of MeOH. The aromatic benzyl protecting group (11), aromatic chloride and bromide (13 and 11), and epoxide (14) were thoroughly maintained under 3% Pd/SiC-catalyzed hydrogenation conditions (Entries 8–10). tert-Butyldimethylsilyl (TBDM) ether (15) was also resistant to the hydrogenation conditions, whereas the alkene was selectively hydrogenated within 1 h (16, Entry 11).

Table 1. Scope of applicable substrates under batch-reaction conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield a (Time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td>quant. (3 h)</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td>quant. (6 h)</td>
</tr>
<tr>
<td>3</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td>quant. (4 h)</td>
</tr>
<tr>
<td>4 b</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td>quant. (4 h)</td>
</tr>
<tr>
<td>Ref</td>
<td>Structure</td>
<td>Yield</td>
<td>Reaction Conditions</td>
</tr>
<tr>
<td>-----</td>
<td>-----------</td>
<td>-------</td>
<td>---------------------</td>
</tr>
<tr>
<td>5c</td>
<td><img src="image1" alt="Structure" /></td>
<td>n.r.</td>
<td>(quant.) (24 h)</td>
</tr>
<tr>
<td>6c</td>
<td><img src="image2" alt="Structure" /></td>
<td>n.r.</td>
<td>(quant.) (24 h)</td>
</tr>
<tr>
<td>7c</td>
<td><img src="image3" alt="Structure" /></td>
<td>n.r.</td>
<td>(quant.) (24 h)</td>
</tr>
<tr>
<td>8</td>
<td><img src="image4" alt="Structure" /></td>
<td>n.r.</td>
<td>(quant.) (24 h)</td>
</tr>
<tr>
<td>9</td>
<td><img src="image5" alt="Structure" /></td>
<td>n.r.</td>
<td>(quant.) (24 h)</td>
</tr>
<tr>
<td>10</td>
<td><img src="image6" alt="Structure" /></td>
<td>n.r.</td>
<td>(97%) (24 h)</td>
</tr>
<tr>
<td>11</td>
<td><img src="image7" alt="Structure" /></td>
<td>n.r.</td>
<td>(quant.) (1 h)</td>
</tr>
</tbody>
</table>

* Isolated yield. The recovery rate of the substrate is indicated in parentheses. ** At 50 °C. *** EtOAc was used as the solvent instead of MeOH. n.r.: no reaction.

The catalytic activity of 3% Pd/SiC is shown in Figure 1. The alkyne, alkene, azide, nitro, and aromatic N-Cbz functionalities were chemoselectively hydrogenated. However, alkyl N-Cbz, benzyl ether, aromatic ketone, benzyl ester, epoxide, aromatic chloride, bromide, and TBDMS ether were tolerant to 3% Pd/SiC-catalyzed hydrogenation.

![Figure 1](image8)

Next, the reusability of 3% Pd/C was investigated. 3% Pd/SiC was recovered and reused at least three times without loss of catalytic activity, and the hydrogenated product (18) was nearly quantitatively obtained (Table 2). Furthermore, Pd species were not detected in the filtrate by AAS after the 3% Pd/SiC-catalyzed hydrogenation of 17 (Pd detection limit: 1 ppm, Scheme 1).
Table 2. Reuse test of 3% Pd/SiC.

<table>
<thead>
<tr>
<th>Run</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (%)</td>
<td>99</td>
<td>quant.</td>
<td>97</td>
</tr>
<tr>
<td>Catalyst recovery yield (%)</td>
<td>99</td>
<td>quant.</td>
<td>95</td>
</tr>
</tbody>
</table>

Scheme 1. Pd-leaching test.

The physical properties of 3% Pd/SiC before and after use were determined by focused ion beam scanning electron microscopy (FIB-SEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS). The mean particle size of the Pd clusters on the catalyst was estimated to be approximately 30–40 nm and distributed on the surface of 3% Pd/SiC (Figure 2a–d). Sintering of some parts of the Pd clusters was observed after hydrogenation (Figure 2c vs. Figure 2d). EDX analysis confirmed the presence of Pd on SiC before and after use (Figure 2e,f). The detailed FIB-SEM and EDX images are also provided in Supplementary Materials. The results of XPS analysis (Figure 2g,h) indicated that the 3% Pd/SiC catalyst clearly consisted of a combination of Pd(0) (characteristic peaks at ca. 341.0 and 335.7 eV, corresponding to Pd\(^{0}\)\(^{3d_{3/2}}\) and Pd\(^{0}\)\(^{3d_{5/2}}\), respectively) and Pd(II) (characteristic peaks at ca. 342.9 and 337.7 eV, corresponding to Pd\(^{II}\)\(^{3d_{3/2}}\) and Pd\(^{II}\)\(^{3d_{5/2}}\), respectively) species. The ratio of Pd(0) to Pd(II) in 3% Pd/SiC before hydrogenation was approximately 3:2 but changed to approximately 2:1 after the reaction, and the ratio of Pd (0) slightly increased. The detailed area percentages of the Pd(0) and Pd(II) species are provided in the Supplementary Materials (Figure S1). Therefore, the Pd(II) species on 3% Pd/SiC were partially reduced to Pd(0) and sintered during the hydrogenation reaction, while the hydrogenation catalyst activity was maintained regardless of the state of the Pd species.
Due to probably the 30–40 nm cluster formation of the mixture of 0 and II valent Pd metals, 3% Pd/SiC possesses a reasonably lower catalyst activity. Akyne, alkene, azide, nitro, and aromatic N-Cbz functionalities could be selectively hydrogenated. Next, we developed a semihydrogenation catalyst for alkynes utilizing the relatively mild hydrogenation catalyst activity of 3% Pd/SiC. First, we determined the optimal reaction conditions, such as solvents and amine-based additives (Supplementary Materials, Table S1). After detailed investigations using 1a as the substrate, diethylenetriamine (DETA) was found to be a suitable additive for the semihydrogenation of 1a (Table S1, Entry 5). Various di-
and monosubstituted alkynes were used as substrates for the 3% Pd/SiC-catalyzed semi-
hydrogenation reaction (Table 3).

Table 3. Semihydrogenation of alkynes under batch-reaction conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Product</th>
<th>Time (h)</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
<th>E/Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="Image" /></td>
<td>2</td>
<td>98</td>
<td>93 [52] ▲ (2/98)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="Image" /></td>
<td>24</td>
<td>100</td>
<td>93 (1/99)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="Image" /></td>
<td>4</td>
<td>100</td>
<td>95 (2/98)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td><img src="image" alt="Image" /></td>
<td>4</td>
<td>99</td>
<td>97 (85) ▲ (2/98)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td><img src="image" alt="Image" /></td>
<td>2</td>
<td>100</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td><img src="image" alt="Image" /></td>
<td>1.5</td>
<td>100</td>
<td>90</td>
<td></td>
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<tr>
<td>7</td>
<td><img src="image" alt="Image" /></td>
<td>6</td>
<td>99</td>
<td>99</td>
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<tr>
<td>8</td>
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<td>2</td>
<td>100</td>
<td>67</td>
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</tr>
<tr>
<td>9</td>
<td><img src="image" alt="Image" /></td>
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<td>98</td>
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<td>10</td>
<td><img src="image" alt="Image" /></td>
<td>0.75</td>
<td>85</td>
<td>84</td>
<td></td>
</tr>
</tbody>
</table>
The semihydrogenation of disubstituted alkynes (1a–1c) proceeded efficiently with the combined use of 3% Pd/SiC (1 mol%) and DETA (1.5 eq.) to give the corresponding Z-alkenes (2a–c) with high conversion (>99%), yields (93–97%) and excellent Z-selectivities (E/Z = 2/98, Entries 1, 3, and 4). 2a and 2c were isolated by recrystallization in 52% and 85% yield, respectively. The high yield (93%) and Z-selectivity (E/Z = 1/99) of 2a were maintained after 24 h (Entry 2). Furthermore, monosubstituted alkynes, such as 2-ethyl-6-methoxynaphthalene (1d) and N-Cbz-protected 4-ethynyl aniline (1e), were quantitatively transformed into their corresponding styrene derivatives (2d and 2e) in 96% and 90% yields, respectively (Entries 5 and 6). The semihydrogenation of 4-acetyl phenylacetylene (1f) proceeded to give 4-acetyl styrene (2f) in 99% yield when ethylenediamine [54–56] was used instead of DETA as an additive (Entry 7). The isolated yield of 4-aminostyrene (2g) was relatively low (67%), which could be due to the disturbance of the coordination of DETA to Pd species by the competitive coordination of the aromatic amino groups of the substrate (2g) and product (2g) during hydrogenation (Entry 8). A new complex catalyst [3% Pd(DETA)/SiC] in which DETA was immobilized on heterogeneous 3% Pd/SiC to avoid its competitive coordination to Pd species, was then prepared by the simple mixing of 3% Pd/SiC and 70 equivalents of DETA at 25 °C for 7 days [56]. The 3% Pd(DETA)/SiC was an effective catalyst, resulting in 2g in 92% yield (Entry 9). DETA was not detected from the crude reaction mixture after Pd(DETA)/SiC-catalyzed hydrogenation of 1a (Scheme 2). The original 3% Pd/SiC catalyst could also be applied to the chemoselective semihydrogenation of 4-nitroethynylbenzene (1h), which possesses alkyne and nitro groups within the molecule, to give 4-nitrostyrene (2h) in 84% yield (Entry 10). Ethynylestradiol (1i), an estrogen receptor agonist, was partially hydrogenated using 3% Pd/SiC and DETA to give the corresponding 2i in 96% yield (Entry 11).

![Scheme 2](image-url)
Semihydrogenation of mono- and disubstituted alkynes were nearly completed during the residence time of 1 to 2 min (The calculation of residence time was indicated in Supplementary Materials).

**Table 4.** Semihydrogenation of alkynes under continuous-flow conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Product</th>
<th>Residence Time</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Image" /></td>
<td>1 min</td>
<td>97</td>
<td>90 [44] c (2/98)</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2.png" alt="Image" /></td>
<td>2 min</td>
<td>97</td>
<td>91 (2/98)</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3.png" alt="Image" /></td>
<td>2 min</td>
<td>10</td>
<td>95 (83) c (3/97)</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4.png" alt="Image" /></td>
<td>1 min</td>
<td>96</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5.png" alt="Image" /></td>
<td>1 min</td>
<td>100</td>
<td>82</td>
</tr>
<tr>
<td>6</td>
<td><img src="image6.png" alt="Image" /></td>
<td>2 min</td>
<td>100</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td><img src="image7.png" alt="Image" /></td>
<td>1 min</td>
<td>100</td>
<td>87</td>
</tr>
<tr>
<td>8</td>
<td><img src="image8.png" alt="Image" /></td>
<td>1 min</td>
<td>93</td>
<td>92</td>
</tr>
</tbody>
</table>

* Reaction conditions: 3% Pd/SiC (1 mol%), alkyne (1, 0.25 mmol), H₂ (balloon), MeOH (0.25 M) at 25 °C. b Determined by ¹H NMR using ethylene carbonate as the internal standard. c Isolated yield.
At a flow rate of 0.05 mL/min. A solution of DETA (0.25 M) in MeOH was pumped into the catalyst cartridge at a flow rate of 0.3 mL/min for 30 min, followed by a solution of 1f and DETA (5.0 eq.).

Next, the continuous-flow semihydrogenation reaction of 1c over time was investigated under 3% Pd/SiC-prepacked-cartridge conditions (Figure 3, dashed line with red circles). The catalytic activity of the system remained high during the first 3 h, but significantly declined after 3 h. The yield of 2c decreased to 65% after 24 h (red squares), accompanied by the remaining unchanged 1c (34%, red circles). The degradation of catalyst activity could be induced by the continuous flow of excess amounts of DETA as the coordinating agent of 3% Pd/SiC, which strongly coordinates with 3% Pd/SiC during the flow reaction. The use of a catalyst cartridge filled with 3% Pd(DETA)/SiC without the addition of DETA dramatically improved the catalyst activity of the system over 24 h (solid line with blue circles). The 1c was nearly quantitatively semihydrogenated (blue circles), and the corresponding 2c was continuously generated over 24 h in excellent yield (ca. 90%, blue squares). The detailed results were indicated in Supplementary Materials (Tables S4 and S5).

Figure 3. Long-term continuous-flow semihydrogenation of 1c with 3% Pd/SiC and 3% Pd(DETA)/SiC.

3. Materials and Methods
3.1. Materials

All reagents and solvents were obtained from commercial sources and used without further purification. Silicon carbide was obtained from Cataler Corporation (Shizuoka, Japan). Pd(OAc)₂ was obtained from N.E. Chemcat Corporation (Tokyo, Japan). The ¹H NMR and ¹³C NMR spectra were recorded on JEOL JNM ECA-500 (500 MHz for ¹H NMR
and 125 MHz for $^{13}$C NMR) and ECZ-400 (400 MHz for $^1$H NMR and 100 MHz for $^{13}$C NMR) spectrometers. CDCl$_3$ was used as the solvent for the NMR measurements. The chemical shifts (δ) are expressed in parts per million and internally referenced (0.00 ppm for tetramethylsilane and 77.0 ppm for CDCl$_3$ for $^{13}$C NMR). FlowFactory Flow reactor FX-1000G (EYELA) was used for the continuous-flow hydrogenation reactions. Thermo Fisher Helios G4 PFIB UX, ULVAC-PHI QuanteraSXM, OXFORD X-MaxN 150 and Shimadzu AA-7000 instruments were used for focused ion beam scanning electron microscopy (FIB-SEM) analysis, X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectrometry (EDX), and atomic absorption spectrometry (AAS), respectively. All of the $^1$H NMR spectra of the known products were identical to those reported in the literature.

3.2. Preparation of Catalyst

Preparation of 3% Pd/SiC (Scheme 3): Pd species were supported on SiC according to our previously established heterogeneous catalyst preparation method [70,71]. Cubic SiC (grayish color) was crushed to small particles by using a mortar and pestle, passed through a filter (diameter of the filter is <63 µm), and deaerated in vacuo. A solution of Pd(OAc)$_2$ [39.1 mg, 174.1 µmol (18.5 mg, palladium quantity)] in MeOH (6.0 mL) was poured into SiC particles (600 mg) placed in a 50 mL-round-bottom flask and stirred under argon atmosphere at 25 °C for 24 h. The resulting dark gray solid was collected by filtration (1.0 µm filter paper), washed with H$_2$O (10 mL × 3) and MeOH (10 mL × 3), and dried in vacuo for 24 h to give Pd/SiC (608.5 mg). The filtrate was transferred to a 100 mL volumetric flask and diluted to 100 mL with MeOH; 7.2 ppm (0.7 mg) of palladium species was observed in the diluted filtrate by using AAS (SHIMADZU AA-7000; Pd detection limit: 1 ppm). The total palladium species that was not absorbed in SiC was 0.7 mg; thus, the palladium content of Pd/SiC was estimated to be approximately 3% \(\left(\frac{18.5 - 0.7}{600 + 18.5 - 0.7} \times 100\right)\).

**Scheme 3.** Preparation of 3% Pd/SiC.

Preparation of 3% Pd(DETA)/SiC (Scheme 4): A suspension of 3% Pd/SiC [100 mg, 25.3 µmol (2.7 mg, palladium quantity)] and DETA (191.0 µL, 1.77 mmol) in MeOH (1.0 mL) was stirred under argon atmosphere at 25 °C for 7 d. The resulting dark gray solid was collected by filtration (1 µm filter paper), washed with MeOH (5 mL × 3) and Ether (5 mL × 3), and dried in vacuo for 24 h to give Pd(DETA)/SiC (98.7 mg). The filtrate was transferred to a 50 mL volumetric flask and diluted to 50 mL with MeOH; 0.02 ppm (2.0 µg) of palladium species was observed in the diluted filtrate using AAS (SHIMADZU AA-7000). The total palladium species that was leaked from Pd/SiC was 2.0 µg; thus, the palladium contents of Pd(DETA)/SiC were estimated to be approximately 3% \(\left(\frac{2.7 - 0.002}{100 - 0.002} \times 100\right)\).

**Scheme 4.** Preparation of 3% Pd(DETA)/SiC.
3.3. General Procedure for Hydrogenation Reactions

General procedure for chemoselective hydrogenation under batch conditions (Table 1): A mixture of the substrate (250 µmol) and 3% Pd/SiC (8.8 mg, 2.5 µmol) in MeOH or EtOAc (1.0 mL) was stirred at 25 or 50 °C using a test tube equipped with an H₂ balloon. The reaction was continuously monitored by thin-layer chromatography. After a specific time, as indicated in Table 1, the mixture was filtered by a membrane filter (pore size: 0.45 µm). The catalyst on the filter was washed with diethyl ether (5 mL × 3). The combined filtrates were concentrated in vacuo to afford the corresponding analytically pure product. If necessary, the product was further purified by silica-gel column chromatography (hexane/EtOAc or hexane/diethyl ether).

Reuse test of 3% Pd/SiC (Table 2): A mixture of cinnamyl alcohol (17, 1.07 g, 8.0 mmol) and 3% Pd/SiC (293.8 mg, 80.0 µmol) in MeOH (32 mL) was stirred under an H₂ atmosphere (balloon). After 4 h, the mixture was filtered through a funnel (1 mm filter paper). The catalyst on the filter was washed with EtOAc (3 mL × 5), and the filtrate was concentrated in vacuo to afford 3-phenylpropanol (18). The catalyst on the filter was dried in vacuo at room temperature overnight and then weighed. The reaction for the second run was carried out in a procedure similar to the first run except for the amount of cinnamyl alcohol (1.01 mg, 7.5 mmol) and 3% Pd/SiC (275.2 mg, 75.0 µmol) for 4 h. The reaction for the third run was also carried out likewise the first run except for the usage of substrate and catalyst.

General procedure for semihydrogenation of alkynes under batch conditions (Table 3): A mixture of the substrate (250 µmol), 3% Pd/SiC (8.8 mg, 2.5 µmol), and DETA (40.5 µL, 375 µmol) in MeOH (1.0 mL) was stirred at 25 °C using a test tube equipped with an H₂ balloon. The reaction was continuously monitored by thin-layer chromatography. After a specific time, as indicated in Table 3, the mixture was filtered by a membrane filter (pore size: 0.45 µm). The catalyst on the filter was washed with diethyl ether (5 mL × 3). The combined filtrates were washed with saturated NH₄Cl aq. (3 mL × 3) and brine (3 mL × 1) if additive was used, dried over Na₂SO₄, and concentrated in vacuo to afford the corresponding alkenes with small amounts of substrates and/or alkanes.

General procedure for chemoselective hydrogenation under continuous-flow conditions (Table 4): A solution of the substrate (500 µmol) and DETA (162.0 µL, 1.5 mmol) in MeOH (10 mL, 0.05 M) was pumped into the 3% Pd/SiC (50 mg) catalyst-packed cartridge [φ 5 × 50 mm, stainless] at a flow rate of 0.1 mL/min together with hydrogen gas at a flow rate of 10 mL/min at 25 °C after introducing a flow of MeOH and hydrogen gas into the cartridge under the same condition for ca. 5 min. The cartridge was washed with MeOH (10 mL) and CH₂Cl₂ (10 mL), and the combined reaction mixture was collected and concentrated in vacuo. The solution was added to water (3 mL) and extracted with n-Hexane/AcOEt = 1/1 (6 mL × 3), dried over Na₂SO₄, and concentrated in vacuo to afford the corresponding alkenes with small amounts of substrates and/or alkanes.

Procedure for semihydrogenation of 1c using the combination of 3% Pd/SiC and DETA under continuous-flow conditions (Figure 3): A solution of 1c (511.9 mg, 3.6 mmol) and DETA (1.2 mL, 10.8 mmol) in MeOH (72 mL, 0.05 M) was pumped into the 3% Pd/SiC (50 mg) catalyst-packed cartridge [φ 5 × 50 mm, stainless] at a flow rate of 0.05 mL/min together with hydrogen gas at a flow rate of 10 mL/min at 25 °C after introducing a flow of MeOH and hydrogen gas into the cartridge under the same condition for ca. 5 min. The reaction solution was collected 5 times at 3 h, 6 h, 12 h, 18 h, and 24 h with changing a receiving vessel. The cartridge was washed with MeOH (10 mL) and CH₂Cl₂ (10 mL) and combined with the final solution collected 24 h later. Each reaction solution (1st: 0–3 h, 2nd: 3–6 h, 3rd: 6–12 h, 4th: 12–18 h, and 5th: 18–24 h) was separately added water (3 mL) and extracted with n-Hexane/AcOEt = 1/1 (6 mL × 3), dried over Na₂SO₄, and concentrated in vacuo to afford the corresponding 2c. The yield of 2c and 1c was determined by ¹H NMR using ethylene carbonate (39.6 mg, 0.45 mmol) as an internal standard based on the total theoretical amount of materials on every vessel.
Procedure for semihydrogenation of 1c using the 3% Pd(DETA)/SiC under continuous-flow conditions (Figure 3): A solution of 1c (511.9 mg, 3.6 mmol) in MeOH (72 mL, 0.05 M) was pumped into the 3% Pd(DETA)/SiC (50 mg) catalyst-packed cartridge [φ 5 × 50 mm, stainless] at a flow rate of 0.05 mL/min together with hydrogen gas at a flow rate of 10 mL/min at 25 °C after introducing a flow of MeOH and hydrogen gas into the cartridge under the same condition for ca. 5 min. The reaction solution was collected 5 times at 3 h, 6 h, 12 h, 18 h, and 24 h with changing a receiving vessel. The cartridge was washed with MeOH (10 mL) and CH2Cl2 (10 mL) and combined with the final solution collected 24 h later. Each reaction solution (1st: 0–3 h, 2nd: 3–6 h, 3rd: 6–12 h, 4th: 12–18 h, 5th: 18–24 h) was separately concentrated in vacuo to afford the corresponding 2c. The yield of 2c and 1c was determined by 1H NMR using ethylene carbonate (39.6 mg, 0.45 mmol) as an internal standard based on the total theoretical amount of materials on every vessel.

3.4. Spectroscopic Data of Products

Diphenylethane (Table 1 Entry 1) [CAS Reg. No. 103-29-7]. Obtained in quantitative yield (45.3 mg, 0.25 mmol; colorless solid) from diphenylacetylene (44.6 mg, 0.25 mmol). 1H NMR [500 MHz (ECA-500, CDCl3)] δ 7.28 (4H, dd, J = 7.5, 7.5 Hz), 7.19 (6H, m), 2.92 (4H, s); 13C NMR [125 MHz (ECA-500, CDCl3)] δ 141.7, 128.4, 128.3, 125.8, 37.9. Spectroscopic data of 1H NMR was identical to that of the reference [73].

p-Ethylaniline (Table 1, Entry 2 and 3) [CAS Reg. No. 589-16-2]. Obtained in quantitative yield (30.6 mg, 0.25 mmol; yellow liquid) from p-ethylaniline (37.8 mg, 0.25 mmol). 1H NMR [400 MHz (ECZ-400, CDCl3)] δ 6.89 (2H, d, J = 8.0 Hz), 6.62 (2H, d, J = 6.5 Hz), 3.52, 2.54 (2H, brs), 1.18 (3H, t, J = 7.6 Hz); 13C NMR [100 MHz (ECZ-400, CDCl3)] δ 143.9, 134.4, 128.5, 115.2, 27.9, 15.9. Spectroscopic data of 1H NMR was identical to that of the reference [74].

4-tert-Butylaniline (Table 1, Entry 4) [CAS Reg. No. 769-92-6]. Obtained in quantitative yield (31.0 mg, 0.25 mmol; brown liquid) from N-Cbz-4-tert-butylaniline (36.8 mg, 0.25 mmol). 1H NMR [500 MHz (ECA-500, CDCl3)] δ 7.18 (2H, d, J = 8.5 Hz), 6.23 (2H, d, J = 8.5 Hz), 3.54 (2H, brs), 1.27 (9H, s); 13C NMR [125 MHz (ECA-500, CDCl3)] δ 143.7, 141.3, 125.9, 114.8, 33.8, 31.4. Spectroscopic data of 1H NMR was identical to that of the reference [75].

Benzyl phenethylcarbamate (Table 1, Entry 5) [CAS Reg. No. 70867-38-8]. Obtained in quantitative yield (64.3 mg, 0.25 mmol; pale yellow liquid) from benzyl phenethylcarbamate (63.8 mg, 0.25 mmol). 1H NMR [500 MHz (ECA-500, CDCl3)] δ 7.36–7.16 (10H, m), 5.08 (2H, s), 4.80 (1H, brs), 3.45 (2H, m), 2.80 (2H, t, J = 7.3 Hz); 13C NMR [125 MHz (ECA-500, CDCl3)] δ 156.2, 138.6, 136.4, 128.7, 128.5, 128.4, 128.0, 66.5, 42.1, 35.9. Spectroscopic data of 1H NMR was identical to that of the reference [76].

2,2-Dimethylpropiophenone (Table 1, Entry 6) [CAS Reg. No. 938-16-9]. Obtained in quantitative yield (40.8 mg, 0.25 mmol; colorless liquid) from 2,2-dimethylpropiophenone (40.6 mg, 0.25 mmol). 1H NMR [400 MHz (ECZ-400, CDCl3)] δ 7.69–7.67 (2H, m), 7.47–7.37 (3H, m), 1.35 (9H, s); 13C NMR [100 MHz (ECZ-400, CDCl3)] δ 209.2, 138.4, 130.7, 127.9, 127.7, 44.1, 27.9. Spectroscopic data of 1H NMR was identical to that of the reference [77].

Benzyl-4-bromobenzoate (Table 1, Entry 7) [CAS Reg. No. 120-51-4]. Obtained in quantitative yield (73.4 mg, 0.25 mmol; yellow liquid) from benzyl-4-bromobenzoate (72.8 mg, 0.25 mmol). 1H NMR [500 MHz (ECA-500, CDCl3)] δ 7.92 (2H, d, J = 7.5 Hz), 7.56 (3H, d, J = 7.5 Hz), 7.44–7.33 (5H, m), 5.35 (2H, s); 13C NMR [125 MHz (ECA-500, CDCl3)] δ 165.3, 135.5, 131.4, 130.9, 128.7, 128.4, 128.1, 128.0, 114.8, 66.6. Spectroscopic data of 1H NMR was identical to that of the reference [78].

Benzyl phenyl ether (Table 1, Entry 8) [CAS Reg. No. 946-80-5]. Obtained in quantitative yield (46.4 mg, 0.25 mmol; colorless liquid) from benzyl phenyl ether (46.4 mg, 0.25 mmol). 1H NMR [500 MHz (ECA-500, CDCl3)] δ 7.34 (2H, d, J = 7.5 Hz), 7.32–7.26 (3H, m), 1.35 (9H, s); 13C NMR [100 MHz (ECA-500, CDCl3)] δ 158.7, 136.9, 129.4, 128.5, 127.8, 127.4, 120.8, 114.7, 69.8. Spectroscopic data of 1H NMR was identical to that of the reference [79].
1-Chloronaphthalene (Table 1, Entry 9) [CAS Reg. No. 90-13-1]. Obtained in quantitative yield (41.0 mg, 0.25 mmol; brown liquid) from 1-chloronaphthalene (40.6 mg, 0.25 mmol). \(^1\)H NMR [500 MHz (ECA-500, CDCl\(_3\))] \(\delta\) 8.26 (1H, d, \(J = 8.0\) Hz), 7.82 (1H, d, \(J = 8.0\) Hz), 7.72 (1H, d, \(J = 8.0\) Hz), 7.58–7.49 (3H, m), 7.34 (1H, m); \(^13\)C NMR [125 MHz (ECA-500, CDCl\(_3\))] \(\delta\) 134.4, 131.8, 130.7, 128.1, 127.1, 127.0, 126.6, 126.1, 125.6, 124.3. Spectroscopic data of \(^1\)H NMR was identical to that of the reference [80].

1, 2-Epoxydodecane (Table 1, Entry 10) [CAS Reg. No. 2855-19-8]. Obtained in 97% (recovery) yield (44.8 mg, 0.24 mmol; colorless liquid) from 1, 2-Epoxydodecane (46.1 mg, 0.25 mmol). \(^1\)H NMR [500 MHz (ECA-500, CDCl\(_3\))] \(\delta\) 2.92–2.89 (1H, m), 2.74 (1H, dd, \(J = 4.5, 4.5\) Hz), 2.46 (1H, dd, \(J = 4.5, 2.0\) Hz), 1.53–1.26 (18H, m), 0.88 (3H, \(t, J = 7.5\) Hz); \(^13\)C NMR [125 MHz (ECA-500, CDCl\(_3\))] \(\delta\) 52.3, 47.0, 32.4, 31.8, 29.5, 29.5, 29.4, 29.2, 25.9, 22.6, 14.0. Spectroscopic data of \(^1\)H NMR was identical to that of the reference [81].

1-(tert-Butyldimethylsilyl)oxy-3-phenylpropane (Table 1, Entry 11) [CAS Reg. No. 69404-95-1]. Obtained in quantitative yield (62.8 mg, 0.25 mmol; colorless liquid) from tert-butyl(cinnamyl oxy)dimethysilane (62.1 mg, 0.25 mmol). \(^1\)H NMR [500 MHz (ECA-500, CDCl\(_3\))] \(\delta\) 7.28 (2H, m), 7.20–7.16 (3H, m), 3.64 (2H, \(t, J = 6.1\) Hz), 2.67 (2H, \(t, J = 8.0\) Hz), 1.84 (2H, \(tt, J = 6.1, 8.0\) Hz), 0.91 (9H, s), 0.05 (6H, s); \(^13\)C NMR [125 MHz (ECA-500, CDCl\(_3\))] \(\delta\) 142.2, 128.4, 128.2, 125.6, 62.3, 34.4, 32.0, 25.9, 18.3, -5.2. Spectroscopic data of \(^1\)H NMR was identical to that of the reference [82].

3-Phenyl-1-propanol (Table 2) [CAS Reg. No. 122-97-4]. Obtained in 99% yield (1.08 g, 8.0 mmol) from cinnamyl alcohol (1.07 g, 8.0 mmol). \(^1\)H NMR [500 MHz (ECA-500, CDCl\(_3\))] \(\delta\) 7.28–7.25 (2H, m), 7.19–7.16 (3H, m), 3.62 (2H, \(t, J = 6.3\) Hz), 2.68 (2H, \(t, J = 7.8\) Hz), 1.89–1.83 (2H, \(m, \delta\) 135.4, 71.2, 31.6. Spectroscopic data of \(^1\)H NMR was identical to that of the reference [73].

(Z)-1,2-Diphenylethene [CAS Reg. No. 645-49-8]. Table 3, Entry 1: Purification by crystallization with CHCl\(_3\) and hexane at 0 °C to obtain 2a in 52% isolated yield (23.4 mg, 0.13 mmol; colorless solid). Table 4, Entry 1: Purification by crystallization with CHCl\(_3\) and hexane at 0 °C to obtain 2a in 44% isolated yield (39.3 mg, 0.26 mmol; colorless solid). \(^1\)H NMR [400 MHz (ECZ-400, CDCl\(_3\))] \(\delta\) 7.26–7.16 (m, 10H), 6.60 (s, 2H); \(^13\)C NMR [100 MHz (ECZ-400, CDCl\(_3\))] \(\delta\) 137.2, 130.2, 128.8, 128.2, 127.1. Spectroscopic data of \(^1\)H NMR was identical to that of the reference [83].

(Z)-1-(Hex-1-ethyl)-4-methoxybenzene (Table 4, Entry 2) [CAS Reg. No. 146646-32-4]. \(^1\)H NMR [500 MHz (ECA-500, CDCl\(_3\))] \(\delta\) 7.22 (d, \(J = 10.0\) Hz, 2H), 6.87 (d, \(J = 10.0\) Hz, 2H) 6.34 (d, \(J = 12.0\) Hz, 1H), 5.60–5.54 (m, 1H), 3.81 (s, 1H), 2.34–2.30 (m, 2H), 1.46–1.32 (m, 4H), 0.90 (t, \(J = 7.3\) Hz, 3H); \(^13\)C NMR [100 MHz (ECZ-400, CDCl\(_3\))] \(\delta\) 158.0, 131.7, 130.5, 129.9, 128.0, 113.5, 55.2, 32.2, 28.3, 22.4, 14.0. Spectroscopic data of \(^1\)H NMR was identical to that of the reference [84].

(Z)-2,5-Dimethylhex-3-en-2,5-diol [CAS Reg. No. 6177-86-4]. Table 3, Entry 1: Purification by crystallization with CHCl\(_3\) and hexane to obtain 2e in 85% isolated yield (30.6 mg, 0.21 mmol; colorless solid). Table 4, Entry 1: Purification by crystallization with CHCl\(_3\) and hexane to obtain 2e in 83% isolated yield (59.7 mg, 0.42 mmol; colorless solid). \(^1\)H NMR [400 MHz (ECZ-400, CDCl\(_3\))] \(\delta\) 5.35 (s, 2H), 4.29 (br, 2H), 1.40 (s, 12H); \(^13\)C NMR [125 MHz (ECA-500, CDCl\(_3\))] \(\delta\) 135.4, 71.2, 31.6. Spectroscopic data of \(^1\)H NMR was identical to that of the reference [85].

2-Methoxy-6-vinylnaphthalene (Table 4, Entry 4) [CAS Reg. No. 63444-51-9]. \(^1\)H NMR [400 MHz (ECZ-400, CDCl\(_3\))] \(\delta\) 7.71–7.67 (m, 3H), 7.60 (d, \(J = 8.8\) Hz, 1H), 7.13–7.10 (m, 2H), 6.84 (dd, \(J = 17.4, 11.0\) Hz, 1H), 5.81 (d, \(J = 17.4\) Hz, 1H), 5.27 (d, \(J = 11.0\) Hz, 1H), 3.91 (s, 3H); \(^13\)C NMR [100 MHz (ECZ-400, CDCl\(_3\))] \(\delta\) 157.7, 136.9, 134.2, 132.9, 129.5, 128.9, 127.0, 126.2, 123.7, 118.9, 113.1, 105.7, 55.3. Spectroscopic data of \(^1\)H NMR was identical to that of the reference [83].

N-Benzylxoycarbonyl-4-aminostyrene (Table 4, Entry 5) [CAS Reg. No. 227778-64-5]. \(^1\)H NMR [400 MHz (ECA-500, CDCl\(_3\))] \(\delta\) 7.42–7.36 (m, 9H), 6.66 (dd, \(J = 17.3, 11.0\) Hz,
2H), 5.67 (d, J = 17.3 Hz, 1H), 5.21–5.17 (m, 3H); 13C NMR [125 MHz (ECA-500, CDCl3)] δ 153.1, 137.3, 136.0, 135.9, 133.0, 128.6, 128.4, 128.3, 126.9, 118.5, 112.7, 67.1. Spectroscopic data of 1H NMR was identical to that of the reference [86].

1-(4-Vinylphenyl)ethanone (Table 4, Entry 6) [CAS Reg. No. 10537-63-0]. 1H NMR [500 MHz (ECA-500, CDCl3)] δ 7.92 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 6.76 (dd, J = 17.7, 11.1 Hz, 1H), 5.88 (d, J = 17.7 Hz, 1H), 5.40 (d, J = 11.1 Hz, 1H), 2.60 (s, 3H); 13C NMR [125 MHz (ECA-500, CDCl3)] δ 197.6, 142.1, 136.2, 135.9, 128.7, 126.3, 116.7, 26.6. Spectroscopic data of 1H NMR was identical to that of the reference [87].

4-Vinylaniline (Table 4, Entry 7) [CAS Reg. No. 1520-21-4]. 1H NMR [400 MHz (ECZ-400, CDCl3)] δ 7.23 (d, J = 8.8 Hz, 2H), 6.65–6.55 (m, 3H), 5.54 (d, J = 17.2 Hz, 1H) 5.04 (d, J = 10.8 Hz, 1H) 3.69 (br, 2H); 13C NMR [100 MHz (ECZ-400, CDCl3)] δ 146.1, 136.5, 128.3, 127.3, 115.0. Spectroscopic data of 1H NMR was identical to that of the reference [88].

1-Nitro-4-vinylbenzene (Table 3, Entry 10) [CAS Reg. No. 1520-21-4]. 1H NMR [500 MHz (ECA-500, CDCl3)] δ 8.20 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 6.79 (dd, J = 17.5, 11.0 Hz, 1H), 5.94 (d, J = 17.5, 1H), 5.51 (d, J = 11.0 Hz, 1H); 13C NMR [100 MHz (ECZ-400, CDCl3)] δ 147.1, 143.8, 134.9, 126.8, 123.9, 118.6. Spectroscopic data of 1H NMR was identical to that of the reference [89].

17α-Vinyl-1,3,5(10)-estratriene-3,17β-diol (Table 4, Entry 9) [CAS Reg. No. 7678-95-7]. 1H NMR [500 MHz (ECA-500, CD3OD)] δ 7.08 (d, J = 8.3 Hz, 1H), 6.56 (d, J = 8.3 Hz, 1H), 6.50 (s, 1H), 6.13 (dd, J = 17.3, 10.9 Hz, 1H), 5.19 (d, J = 17.3 Hz, 1H), 5.13 (d, J = 10.9 Hz, 1H), 2.86–2.78 (m, 2H), 2.30–2.27 (m, 1H), 2.00–1.89 (m, 4H), 1.79–1.73 (m, 1H), 1.67–1.64 (m, 1H), 1.53–1.41 (m, 6H), 0.96 (s, 3H); 13C NMR [125 MHz (ECA-500, CD3OD)] δ 156.8, 145.5, 140.0, 133.4, 128.0, 116.9, 114.6, 113.1, 85.9, 51.0, 48.7, 46.0, 42.0, 37.2, 34.3, 31.6, 29.6, 28.5, 25.1, 15.6. Spectroscopic data of 1H NMR was identical to that of the reference [73].

4. Conclusions

We developed Pd catalysts supported on silicon carbide [3% Pd/SiC and 3% Pd(DETA)/SiC] for chemoselective hydrogenation. The alkyne, alkene, azide, nitro, and aromatic N-Cbz functionalities were chemoselectively hydrogenated by 3% Pd/SiC, which revealed good reusability for at least three cycles under batch-reaction conditions. By contrast, 3% Pd/SiC did not exhibit catalytic activity toward the hydrogenation of benzyl ether, alkyl N-Cbz, epoxide, aromatic chloride, aromatic ketone, and TBDMS ether. FIB-SEM, EDX, and XPS analyses of 3% Pd/SiC before and after hydrogenation provided further insights into the physicochemical properties of the Pd metal on SiC. The combination of 3% Pd/SiC and DETA showed excellent chemoselectivity for the semihydrogenation of various mono- and disubstituted alkynes under batch- and flow-reaction conditions. The catalyst activity might be properly suppressed via bidentate or tridentate coordination of amino groups of DETA with Pd metals [54–60]. Furthermore, the newly developed 3% Pd(DETA)/SiC-packed in a cartridge demonstrated high chemoselectivity for the continuous-flow semihydrogenation of the alkyne functionality over 24 h. A wide variety of alkene derivatives could be synthesized under ambient temperature and H2 pressure by the 3% Pd/SiC or 3% Pd(DETA)/SiC-catalyzed partial hydrogenation of parent alkynes under batch- and flow-reaction conditions. These catalysts and hydrogenation methods are expected to be attractive tools for synthetic organic and process chemistry.

Supplementary Materials:
The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12101253/s1, Figure S1: XPS spectra of 3% Pd/SiC before and after the reaction; Table S1: Optimization of semihydrogenation reaction under batch conditions; Table S2: Optimization of semihydrogenation reaction under continuous-flow conditions; Table S3: Reuse test of Pd/SiC; Table S4: Long-term Continuous-flow semihydrogenation of 1c using 3% Pd/SiC; Table S5: Long-term Continuous-flow semihydrogenation of 1c using 3% Pd(DETA)/SiC; Content 1: General; Content 2: Preparation of 3% Pd/SiC catalyst (Scheme 3); Content 3: Preparation of catalyst cartridge; Content 4: Preparation of 3% Pd(DETA)/SiC catalyst.
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(Scheme 4); Content 5: General procedure for the scope of the substrate under batch conditions; Content 6: General procedures for semihydrogenation of alkynes under batch and continuous-flow conditions; Content 7: Optimization of semihydrogenation under batch and continuous-flow conditions; Content 8: Reuse test of 3% Pd/SiC; Content 9: FIB-SEM image and EDX analysis of 3% Pd/SiC; Content 10: Long-term continuous-flow semihydrogenation (Figure 3); Content 11: Calculation of the residence time; Content 12: DETA leaching test; Content 13: Spectroscopic data of products, Content 14: 1H and 13C spectra of products.

**Author Contributions:** Writing—original draft and supporting information preparation, T.Y., H.Y., K.K. and K.P.; designing the research, T.Y. and H.S.; investigation, experiment, and analysis, T.Y., H.Y., K.K., K.P. and N.A.; project administration, supervision, funding acquisition, writing—review and editing, H.S. All authors have read and agreed to the published version of the manuscript.

**Funding:** A part of this work is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO, Project code: Pt9004).

**Data Availability Statement:** The Supplementary Materials are available free of charge on the website.

**Acknowledgments:** We thank Cataler Corporation for the kind gift of silicon carbide and N. E. Chemcat Corporation for the gift of palladium(II) acetate.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**


