

Article

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 benzyloxycarbonyl-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*-butyldimethylsilyl 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



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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)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 H₂ 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 H₂ 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 TiO₂ 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 coordinating

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 alkynes.

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 alkynes under ordinary H₂ pressure and ambient temperature. Pd(DETA)/SiC can be used under batch and continuous-flow conditions.

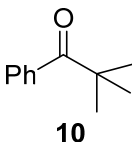
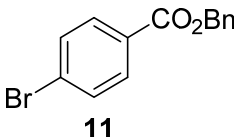
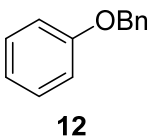
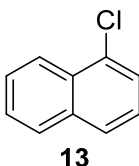
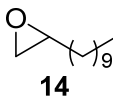
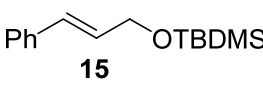
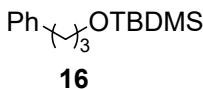
2. Results

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*-benzyloxycarbonyl (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-Dimethylpropiophenone (**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 (TBDMS) 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.

Substrate 0.25 mmol	3%Pd/SiC (1 mol%) MeOH (0.25 M), H ₂ (balloon) 25 °C, Time	Product	
Entry	Substrate	Product	Yield ^a (Time)
1			quant. (3 h)
2			quant. (6 h)
3			quant. (4 h)
4 ^b			quant. (4 h)
5 ^c		n.r.	(quant.) (24 h)

Table 1. Cont.

Substrate	3%Pd/SiC (1 mol%) MeOH (0.25 M), H ₂ (balloon) 25 °C, Time	Product	
Entry	Substrate	Product	Yield ^a (Time)
6 ^c	 10	n.r.	(quant.) (24 h)
7 ^c	 11	n.r.	(quant.) (24 h)
8	 12	n.r.	(quant.) (24 h)
9	 13	n.r.	(quant.) (24 h)
10	 14	n.r.	(97%) (24 h)
11	 15	 16	quant. (1 h)

^a Isolated yield. The recovery rate of the substrate is indicated in parentheses. ^b At 50 °C. ^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.

Catalyst activity of 3% Pd/SiC

Reducible	Irreducible
Alkyne Alkene	Ar-COR Alkyl <i>N</i> -Cbz Ar-O-Bn
R-N ₃ Ar-NO ₂	Ar-CO ₂ Bn Ar-Cl Ar-Br
Aromatic <i>N</i> -Cbz	Epoxide R-O-TBDMS

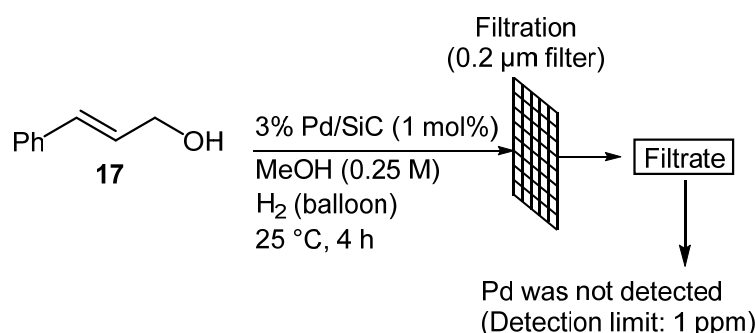
Figure 1. Catalyst activity of 3% Pd/SiC.

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.

$\text{Ph}-\text{CH}=\text{CH}-\text{CH}_2\text{OH} \xrightarrow[\text{25 } ^\circ\text{C, 4 h}]{\text{3\% Pd/SiC (1 mol\%)}, \text{MeOH (0.25 M)}, \text{H}_2 \text{ (balloon)}} \text{Ph}-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ <p style="text-align: center;">17 18</p>			
Run	1st	2nd	3rd
Yield (%)	99	quant.	97
Catalyst recovery yield (%)	99	quant.	95



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 $\text{Pd}^0 3d_{3/2}$ and $\text{Pd}^0 3d_{5/2}$, respectively) and Pd(II) (characteristic peaks at ca. 342.9 and 337.7 eV, corresponding to $\text{Pd}^{\text{II}} 3d_{3/2}$ and $\text{Pd}^{\text{II}} 3d_{5/2}$, 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. Alkyne, 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 semihydrogenation reaction (Table 3).

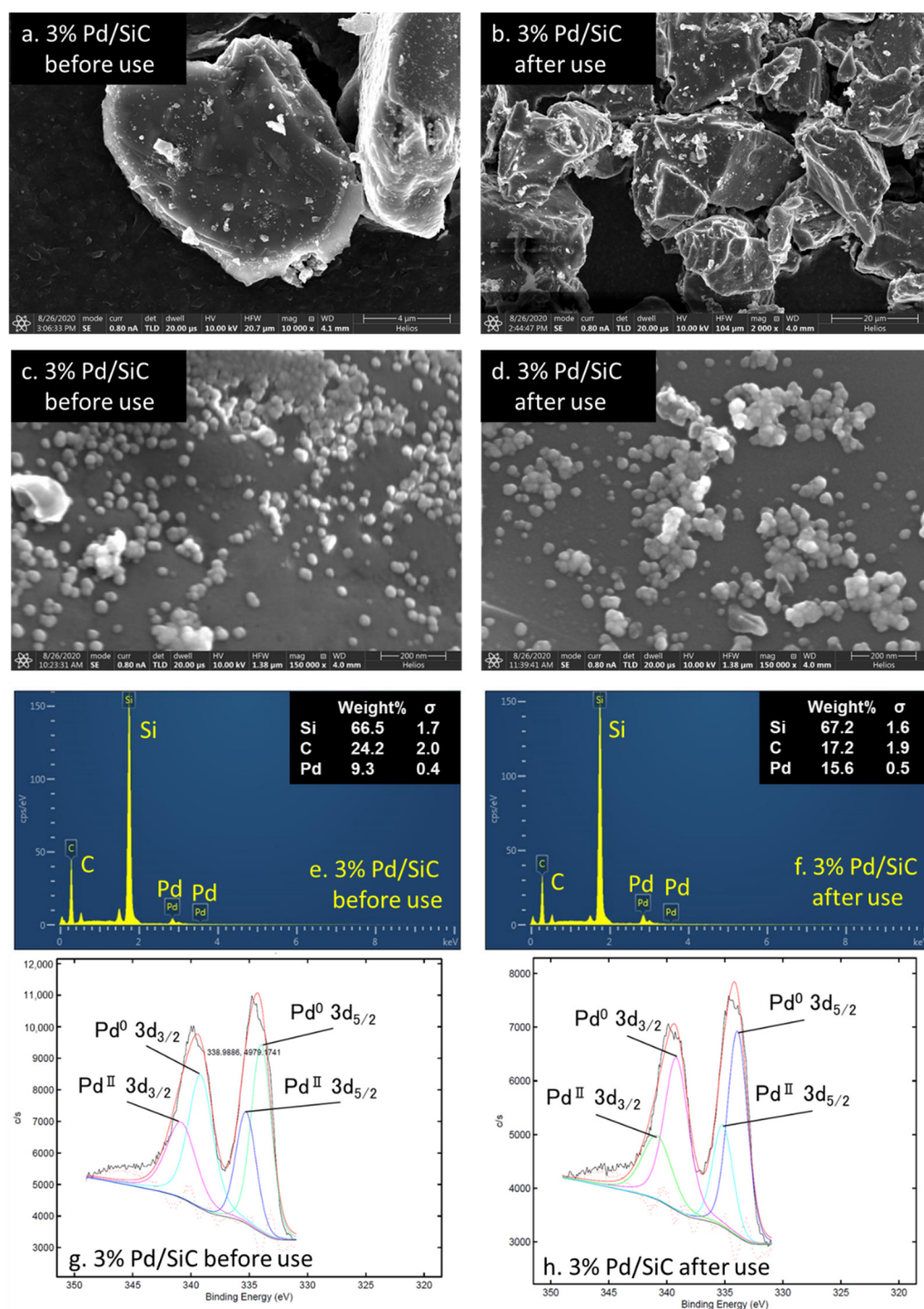


Figure 2. (a–d) FIB-SEM image of 3% Pd/SiC. (e,f) EDX analysis of 3% Pd/SiC. (g,h) XPS spectra of 3% Pd/SiC.

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

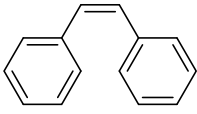
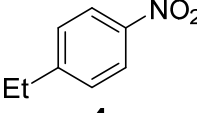
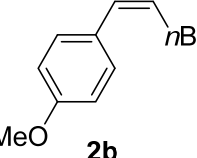
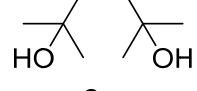
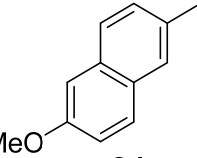
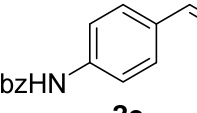
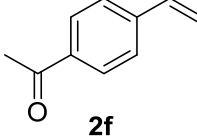
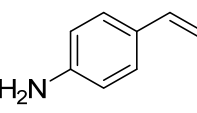
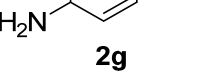
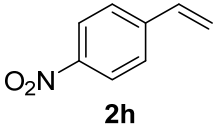
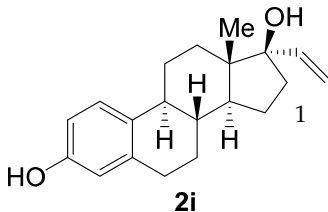
$ \begin{array}{c} \text{R} \text{---} \text{C} \equiv \text{C} \text{---} \text{R}' \\ \text{0.25 mmol} \\ \mathbf{1} \end{array} \xrightarrow[\begin{array}{c} \text{3\% Pd/SiC (1 mol\%)} \\ \text{DETA (1.5 eq.)} \\ \text{MeOH (0.25 M)} \\ \text{H}_2 \text{ (balloon)} \\ \text{25 } ^\circ\text{C, Time} \end{array}]{ \begin{array}{c} \text{R} \text{---} \text{C} = \text{C} \text{---} \text{R}' \\ \mathbf{2} \end{array} } $				
Entry	Product	Time (h)	Conv. (%) ^b	Yield (%) ^b (E/Z)
1	 2a	2	98	93 [52] ^c (2/98)
2	 4	24	100	93 (1/99)
3	 2b	4	100	95 (2/98)
4	 2c	4	99	97 (85) ^c (2/98)
5	 2d	2	100	96
6	 2e	1.5	100	90
7 ^d	 2f	6	99	99
8	 2g	2	100	67
9 ^e	 2g	1	98	92

Table 3. Cont.

$ \begin{array}{c} \text{R} \text{---} \text{C} \equiv \text{C} \text{---} \text{R}' \\ \text{0.25 mmol} \\ \mathbf{1} \end{array} \xrightarrow[\begin{array}{c} \text{MeOH (0.25 M)} \\ \text{H}_2 \text{ (balloon)} \\ 25^\circ\text{C, Time} \end{array}]{ \begin{array}{c} \text{3\% Pd/SiC (1 mol\%)} \\ \text{DETA (1.5 eq.)} \end{array} } \begin{array}{c} \text{R} \text{---} \text{C} = \text{C} \text{---} \text{R}' \\ \mathbf{2} \end{array} $				
Entry	Product	Time (h)	Conv. (%) ^b	Yield (%) ^b (E/Z)
10	 2h	0.75	85	84
11	 2i	1	98	96

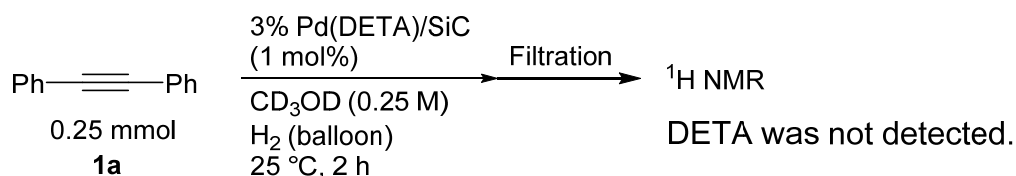
^a Reaction conditions: 3% Pd/SiC (1 mol%), alkyne (**1**, 0.25 mmol), H₂ (balloon), MeOH (0.25 M) at 25 °C.

^b Determined by ¹H NMR using ethylene carbonate as the internal standard. ^c Isolated yield. ^d Ethylenediamine (1.5 eq.) was used instead of DETA (1.5 eq.). ^e Immobilized catalyst 3% Pd(DETA)/SiC was used instead of the combination of 3% Pd/SiC and DETA.

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-ethynyl-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).

Semihydrogenation using 3% Pd/SiC was applied to the continuous-flow reaction, effectively utilizing the solidity and uniformity of the sieved particle size (Table 4). A solution of alkyne (**1**, 0.5 mmol) and DETA (3.0 eq.) in MeOH (0.25 M) was pumped into a catalyst cartridge (50 mg of 3% Pd/SiC) at a flow rate of 0.1 mL/min, together with H₂ (10 mL/min). The optimization of catalyst usage and flow rate were indicated in Supplementary Materials (Table S2). Disubstituted alkynes (**1a–1c**) were continuously semihydrogenated to give the corresponding Z-alkenes (**2a–2c**) with excellent diastereoselectivities and yields, regardless

of the alkyne substituent (Entries 1–3). The continuous-flow semihydrogenation of mono-substituted alkynes (**1d–1h**) afforded the corresponding alkenes (**2d–2h**) in high to excellent yields (80–92%, Entries 4–8). It is noteworthy that 3% Pd/SiC-catalyzed 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).



Scheme 2. DETA leaching test under hydrogenation of **1a**.

Table 4. Semihydrogenation of alkynes under continuous-flow conditions ^a.

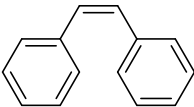
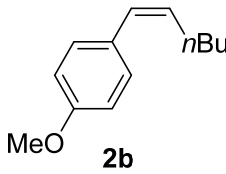
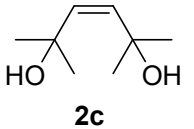
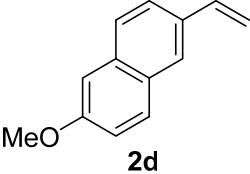

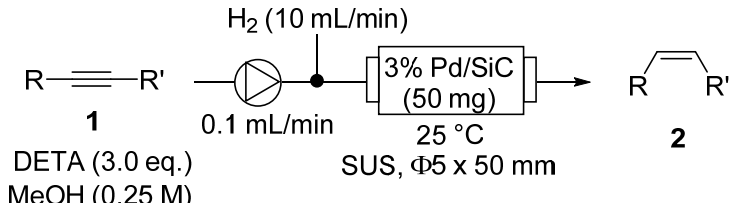
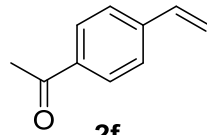
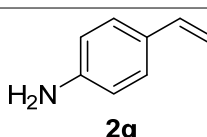
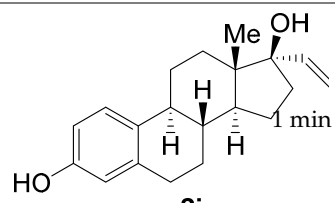
<div style="display: flex; align-items: center; justify-content: center;"> <div style="text-align: center; margin-right: 10px;"> $\text{R}-\text{C}\equiv\text{C}-\text{R}'$ 1 </div> <div style="text-align: center; margin-right: 10px;"> $\xrightarrow[\text{0.1 mL/min}]{\text{H}_2 \text{ (10 mL/min)}}$ </div> <div style="border: 1px solid black; padding: 5px; text-align: center; margin-right: 10px;"> 3% Pd/SiC (50 mg) 25 °C SUS, Φ5 x 50 mm </div> <div style="text-align: center; margin-right: 10px;"> \rightarrow </div> <div style="text-align: center;"> $\text{R}-\text{C}=\text{C}-\text{R}'$ 2 </div> </div> <div style="margin-top: 5px;"> DETA (3.0 eq.) MeOH (0.25 M) </div>				
Entry	Product	Residence Time	Conv. (%) ^b	Yield (%) ^b (E/Z)
1	 2a	1 min	97	90 [44] ^c (2/98)
2 ^d	 2b	2 min	97	91 (2/98)
3 ^d	 2c	2 min	10	95 (83) ^c (3/97)
4	 2d	1 min	96	90
5	 2e	1 min	100	82

Table 4. Cont.

				
Entry	Product	Residence Time	Conv. (%) ^b	Yield (%) ^b (E/Z)
6 ^d	 2f	2 min	100	80
7 ^e	 2g	1 min	100	87
8	 2i	1 min	93	92

^a 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. ^d At a flow rate of 0.05 mL/min. ^e 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).

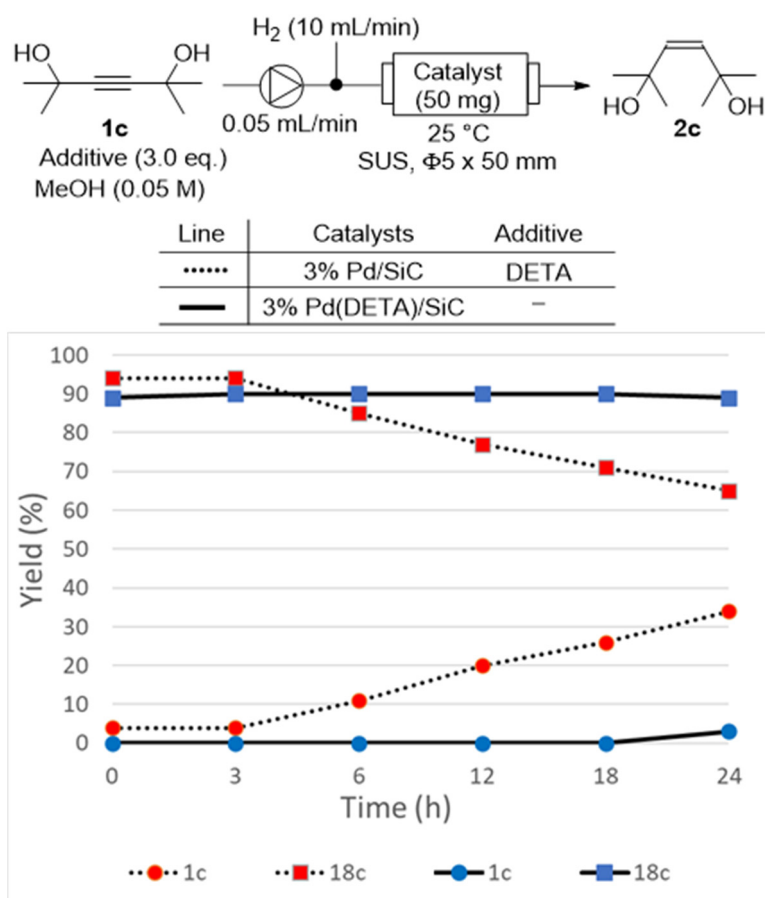


Figure 3. Long-term continuous-flow semihydrogenation of **1c** with 3% Pd/SiC and 3% Pd(DETA)/SiC.

3. Materials and Methods

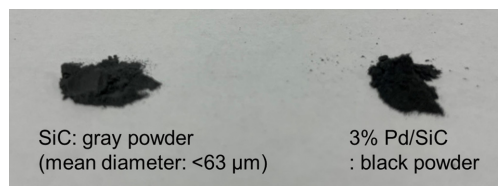
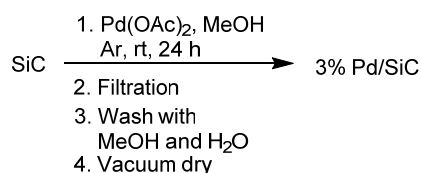
3.1. Materials

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 ¹³C NMR) and ECZ-400 (400 MHz for ¹H NMR and 100 MHz for ¹³C NMR) spectrometers. CDCl₃ 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 CDCl₃ for ¹³C NMR). FlowFactory Flow reactor FFX-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 ¹H NMR spectra of the known products were identical to those reported in the literature.

3.2. Preparation of Catalyst

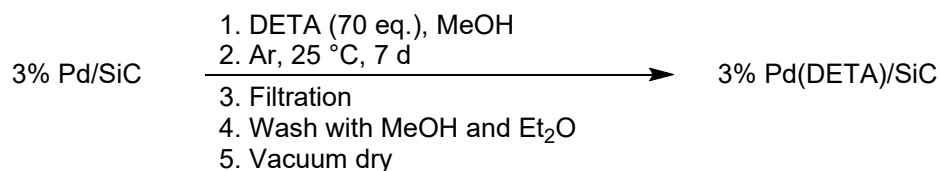
Preparation of 3% Pd/SiC (Scheme 3): Pd species were supported on SiC according to our previously established heterogeneous catalyst preparation method [70,71]. Cubic SiC (grayish color) was crushed to small particles by using a mortar and pestle, passed through a filter (diameter of the filter is <63 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 H₂O (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% [(18.5 – 0.7)/(600 + 18.5 – 0.7) × 100].



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% [(2.7 – 0.002)/(100 – 0.002) × 100].



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 μ mol), 3% Pd/SiC (8.8 mg, 2.5 μ mol), and DETA (40.5 μ L, 375 μ mol) 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 μ m). The catalyst on the filter was washed with diethyl ether (5 mL \times 3). The combined filtrates were washed with saturated NH₄Cl aq. (3 mL \times 3) and brine (3 mL \times 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 μ mol) and DETA (162.0 μ L, 1.5 mmol) in MeOH (10 mL, 0.05 M) was pumped into the 3% Pd/SiC (50 mg) catalyst-packed cartridge [ϕ 5 \times 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 \times 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 \times 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 \times 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 \times 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*-ethylnitrobenzene (37.8 mg,

0.25 mmol) or *p*-ethylphenyl azide (36.8 mg, 0.25 mmol). ^1H NMR [400 MHz (ECZ-400, CDCl_3)] δ 6.89 (2H, d, J = 8.0 Hz), 6.62 (2H, d, J = 8.0 Hz), 3.52 (2H, brs), 2.54 (2H, q, J = 7.6 Hz), 1.18 (3H, t, J = 7.6 Hz); ^{13}C NMR [100 MHz (ECZ-400, CDCl_3)] 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, CDCl_3)] 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); ^{13}C NMR [125 MHz (ECA-500, CDCl_3)] 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, CDCl_3)] 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); ^{13}C NMR [125 MHz (ECA-500, CDCl_3)] δ 156.2, 138.6, 136.4, 128.7, 128.5, 128.4, 128.0, 126.4, 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, CDCl_3)] δ 7.69–7.67 (2H, m), 7.47–7.37 (3H, m), 1.35 (9H, s); ^{13}C NMR [100 MHz (ECZ-400, CDCl_3)] 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, CDCl_3)] 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); ^{13}C NMR [125 MHz (ECA-500, CDCl_3)] δ 165.3, 135.5, 131.4, 130.9, 128.7, 128.4, 128.1, 128.0, 127.9, 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 (46.1 mg, 0.25 mmol). ^1H NMR [500 MHz (ECA-500, CDCl_3)] δ 7.42 (2H, d, J = 7.5 Hz), 7.38–7.35 (2H, m), 7.32–7.26 (3H, m), 6.98–6.93 (3H, m), 5.04 (2H, s); ^{13}C NMR [125 MHz (ECA-500, CDCl_3)] 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). ^1H NMR [500 MHz (ECA-500, CDCl_3)] δ 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)] δ 134.4, 131.8, 130.7, 128.1, 127.1, 127.0, 126.6, 126.1, 125.6, 124.3. Spectroscopic data of ^1H 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). ^1H NMR [500 MHz (ECA-500, CDCl_3)] δ 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)] δ 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 ^1H NMR was identical to that of the reference [81].

1-(*tert*-Butyldimethylsilyloxy)-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(cinnamyloxy)dimethylsilane (62.1 mg, 0.25 mmol). ^1H NMR [500 MHz (ECA-500, CDCl_3)] δ 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)] δ 142.2, 128.4, 128.2, 125.6, 62.3, 34.4, 32.0, 25.9, 18.3, −5.2. Spectroscopic data of ^1H 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; colorless oil) from cinnamyl alcohol (1.07 g, 8.0 mmol). ^1H NMR [500 MHz (ECA-500, CDCl_3)] δ 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); ^{13}C NMR [125 MHz (ECA-500, CDCl_3)] δ 141.6, 128.1, 128.0, 125.5, 61.4, 33.8, 31.7. Spectroscopic data of ^1H 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).

^1H NMR [400 MHz (ECZ-400, CDCl_3)] δ 7.26–7.16 (m, 10H), 6.60 (s, 2H); ^{13}C NMR [100 MHz (ECZ-400, CDCl_3)] δ 137.2, 130.2, 128.8, 128.2, 127.1. Spectroscopic data of ^1H NMR was identical to that of the reference [83].

(Z)-1-(Hex-1-enyl)-4-methoxybenzene (Table 4, Entry 2) [CAS Reg. No. 146646-32-4]. ^1H NMR [500 MHz (ECA-500, CDCl_3)] δ 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)] δ 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 ^1H NMR was identical to that of the reference [84].

(Z)-2,5-Dimethylhex-3-ene-2,5-diol [CAS Reg. No. 6177-86-4]. Table 3, Entry 1: Purification by crystallization with CHCl_3 and hexane to obtain **2c** 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 **2c** in 83% isolated yield (59.7 mg, 0.42 mmol; colorless solid).

^1H NMR [400 MHz (ECZ-400, CDCl_3)] δ 5.35 (s, 2H), 4.29 (br, 2H), 1.40 (s, 12H); ^{13}C NMR [125 MHz (ECA-500, CDCl_3)] δ 135.4, 71.2, 31.6. Spectroscopic data of ^1H NMR was identical to that of the reference [85].

2-Methoxy-6-vinylnaphthalene (Table 4, Entry 4) [CAS Reg. No. 63444-51-9]. ^1H NMR [400 MHz (ECZ-400, CDCl_3)] δ 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)] δ 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 ^1H NMR was identical to that of the reference [83].

N-Benzyloxycarbonyl-4-aminostyrene (Table 4, Entry 5) [CAS Reg. No. 227778-64-5]. ^1H NMR [400 MHz (ECZ-400, CDCl_3)] δ 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); ^{13}C NMR [125 MHz (ECA-500, CDCl_3)] 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, CDCl_3)] 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); ^{13}C NMR [125 MHz (ECA-500, CDCl_3)] 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, CDCl_3)] 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); ^{13}C NMR [100 MHz (ECZ-400, CDCl_3)] δ 146.1, 136.5, 128.3, 127.3, 115.0, 110.0. 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, CDCl_3)] 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 Hz, 1H), 5.51 (d, J = 11.0 Hz, 1H); ^{13}C NMR [100 MHz (ECZ-400, CDCl_3)] 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].

17 α -Vinyl-1,3,5(10)-estratriene-3,17 β -diol (Table 4, Entry 9) [CAS Reg. No. 7678-95-7]. ^1H NMR [500 MHz (ECA-500, CD_3OD)] 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 (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: XPS data of 3% Pd/SiC; Content 11: Long-term continuous-flow semihydrogenation (Figure 3); Content 12: Calculation of the residence time; Content 13: Spectroscopic data of products, Content 14: ¹H and ¹³C spectra of products.

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References

1. Swamy, K.C.K.; Reddy, A.S.; Sandeep, K.; Kalyani, A. Advances in chemoselective and/or stereoselective semihydrogenation of alkynes. *Tetrahedron Lett.* **2018**, *59*, 419–429. [\[CrossRef\]](#)
2. Sharma, D.M.; Punji, B. 3 d Transition Metal-Catalyzed Hydrogenation of Nitriles and Alkynes. *Chem. Asian J.* **2020**, *15*, 690–708. [\[CrossRef\]](#)
3. Lindlar, H. Ein neuer Katalysator für selektive Hydrierungen. *Helv. Chim. Acta* **1952**, *35*, 446–450. [\[CrossRef\]](#)
4. Lindlar, H.; Dubuis, R. Palladium Catalyst for Partial Reduction of Acetylenes. *Org. Synth. Coll.* **1973**, *5*, 880–883.
5. Thiel, N.O.; Kaewmee, B.; Ngoc, T.T.; Teichert, J.F. A Simple Nickel Catalyst Enabling an E-Selective Alkyne Semihydrogenation. *Chem. Eur. J.* **2020**, *26*, 1597–1603. [\[CrossRef\]](#)
6. Zhang, Y.; Karunananda, M.K.; Yu, H.-C.; Clark, K.J.; Williams, W.; Mankad, N.P.; Ess, D.H. Dynamically Bifurcating Hydride Transfer Mechanism and Origin of Inverse Isotope Effect for Heterodinuclear AgRu-Catalyzed Alkyne Semihydrogenation. *ACS Catal.* **2019**, *9*, 2657–2663. [\[CrossRef\]](#)
7. Gramigna, K.M.; Dickie, D.A.; Foxman, B.M.; Thomas, C.M. Cooperative H₂ Activation across a Metal–Metal Multiple Bond and Hydrogenation Reactions Catalyzed by a Zr/Co Heterobimetallic Complex. *ACS Catal.* **2019**, *9*, 3153–3164. [\[CrossRef\]](#)
8. Murugesan, K.; Bheeter, C.B.; Linnebank, P.R.; Spannenberg, A.; Reek, J.N.H.; Jagadeesh, R.V.; Beller, M. Nickel-Catalyzed Stereodivergent Synthesis of E- and Z-Alkenes by Hydrogenation of Alkynes. *ChemSusChem* **2019**, *12*, 3363–3369. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Hancker, S.; Neumann, H.; Beller, M. Development of a Palladium-Catalyzed Process for the Synthesis of Z-Alkenes by Sequential Sonogashira–Hydrogenation Reaction. *Eur. J. Org. Chem.* **2018**, *2018*, 5253–5259. [\[CrossRef\]](#)
10. Gorgas, N.; Brüning, J.; Stöger, B.; Vanicek, S.; Tilset, M.; Veiros, L.F.; Kirchner, K. Efficient Z-Selective Semihydrogenation of Internal Alkynes Catalyzed by Cationic Iron(II) Hydride Complexes. *J. Am. Chem. Soc.* **2019**, *141*, 17452–17458. [\[CrossRef\]](#)
11. Duan, Y.; Ji, G.; Zhang, S.; Chen, X.; Yang, Y. Additive-modulated switchable reaction pathway in the addition of alkynes with organosilanes catalyzed by supported Pd nanoparticles: Hydrosilylation versus semihydrogenation. *Catal. Sci. Technol.* **2018**, *8*, 1039–1050. [\[CrossRef\]](#)
12. Wen, X.; Shi, X.; Qiao, X.; Wu, Z.; Bai, G. Ligand-free nickel-catalyzed semihydrogenation of alkynes with sodium borohydride: A highly efficient and selective process for cis-alkenes under ambient conditions. *Chem. Commun.* **2017**, *53*, 5372–5375. [\[CrossRef\]](#)
13. Gong, D.; Hu, B.; Yang, W.; Kong, D.; Xia, H.; Chen, D. A Bidentate Ru(II)-NC Complex as a Catalyst for Semihydrogenation of Alkynes to (E)-Alkenes with Ethanol. *Organometallics* **2020**, *39*, 862–869. [\[CrossRef\]](#)
14. Ekebergh, A.; Begon, R.; Kann, N. Ruthenium-Catalyzed E-Selective Alkyne Semihydrogenation with Alcohols as Hydrogen Donors. *J. Org. Chem.* **2020**, *85*, 2966–2975. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Yang, J.; Wang, C.; Sun, Y.; Man, X.; Li, J.; Sun, F. Ligand-controlled iridium-catalyzed semihydrogenation of alkynes with ethanol: Highly stereoselective synthesis of E- and Z-alkenes. *Chem. Commun.* **2019**, *55*, 1903–1906. [\[CrossRef\]](#)
16. Kaicharla, T.; Zimmermann, B.M.; Oestreich, M.; Teichert, J.F. Using alcohols as simple H₂-equivalents for copper-catalysed transfer semihydrogenations of alkynes. *Chem. Commun.* **2019**, *55*, 13410–13413. [\[CrossRef\]](#) [\[PubMed\]](#)
17. Liang, H.; Zhang, B.; Ge, H.; Gu, X.; Zhang, S.; Qin, Y. Porous TiO₂/Pt/TiO₂ Sandwich Catalyst for Highly Selective Semihydrogenation of Alkyne to Olefin. *ACS Catal.* **2017**, *7*, 6567–6572. [\[CrossRef\]](#)
18. Shibahara, F.; Mizuno, T.; Shibata, Y.; Murai, T. Transfer Semihydrogenation of Alkynes Catalyzed by Imidazo [1,5-a]pyrid-3-ylidene–Pd Complexes: Positive Effects of Electronic and Steric Features on N-Heterocyclic Carbene Ligands. *Bull. Chem. Soc. Jpn.* **2020**, *93*, 332–337. [\[CrossRef\]](#)
19. Liang, S.; Hammond, G.B.; Xu, B. Supported gold nanoparticles catalyzed cis-selective semihydrogenation of alkynes using ammonium formate as the reductant. *Chem. Commun.* **2016**, *52*, 6013–6016. [\[CrossRef\]](#)
20. Tian, W.-F.; He, Y.-Q.; Song, X.-R.; Ding, H.-X.; Ye, J.; Guo, W.-J.; Xiao, Q. cis-Selective Transfer Semihydrogenation of Alkynes by Merging Visible-Light Catalysis with Cobalt Catalysis. *Adv. Synth. Catal.* **2020**, *362*, 1032–1038. [\[CrossRef\]](#)
21. Das, M.; Kaicharla, T.; Teichert, J.F. Stereoselective Alkyne Hydrohalogenation by Trapping of Transfer Hydrogenation Intermediates. *Org. Lett.* **2018**, *20*, 4926–4929. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Brzozowska, A.; Azofra, L.M.; Zubar, V.; Atodiresei, I.; Cavallo, L.; Rueping, M.; El-Sepelgy, O. Highly Chemo- and Stereoselective Transfer Semihydrogenation of Alkynes Catalyzed by a Stable, Well-Defined Manganese(II) Complex. *ACS Catal.* **2018**, *8*, 4103–4109. [\[CrossRef\]](#)
23. Zhao, C.-Q.; Chen, Y.-G.; Qiu, H.; Wei, L.; Fang, P.; Mei, T.-S. Water as a Hydrogenating Agent: Stereodivergent Pd-Catalyzed Semihydrogenation of Alkynes. *Org. Lett.* **2019**, *21*, 1412–1416. [\[CrossRef\]](#)
24. Bao, H.; Zhou, B.; Jin, H.; Liu, Y. Diboron-Assisted Copper-Catalyzed Z-Selective Semihydrogenation of Alkynes Using Ethanol as a Hydrogen Donor. *J. Org. Chem.* **2019**, *84*, 3579–3589. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Han, X.; Hu, J.; Chen, C.; Yuan, Y.; Shi, Z. Copper-catalysed, diboron-mediated cis-dideuterated semihydrogenation of alkynes with heavy water. *Chem. Commun.* **2019**, *55*, 6922–6925. [\[CrossRef\]](#) [\[PubMed\]](#)
26. Decker, D.; Drexler, H.-J.; Heller, D.; Beweries, T. Homogeneous catalytic transfer semihydrogenation of alkynes—An overview of hydrogen sources, catalysts and reaction mechanisms. *Catal. Sci. Technol.* **2020**, *10*, 6449–6463. [\[CrossRef\]](#)
27. Garduño, J.A.; Arévalo, A.; García, J.J. Bond and small-molecule activation with low-valent nickel complexes. *Dalton Trans.* **2015**, *44*, 13419–13438. [\[CrossRef\]](#)

28. Sorella, G.L.; Sporni, L.; Canton, P.; Coletti, L.; Fabris, F.; Strukul, G.; Scarso, A. Selective Hydrogenations and Dechlorinations in Water Mediated by Anionic Surfactant-Stabilized Pd Nanoparticles. *J. Org. Chem.* **2018**, *83*, 7438–7446. [\[CrossRef\]](#)
29. Choe, K.; Zheng, F.; Wang, H.; Yuan, Y.; Zhao, W.; Xue, G.; Qiu, X.; Ri, M.; Shi, X.; Wang, Y.; et al. Fast and Selective Semihydrogenation of Alkynes by Palladium Nanoparticles Sandwiched in Metal–Organic Frameworks. *Angew. Chem. Int. Ed.* **2020**, *59*, 3650–3657. [\[CrossRef\]](#)
30. Liu, H.-J.; Lo, H.-K.; Copéret, C. Silica-Supported Cu Nanoparticle Catalysts for Alkyne Semihydrogenation: Effect of Ligands on Rates and Selectivity. *J. Am. Chem. Soc.* **2016**, *138*, 16502–16507.
31. Kaeffer, N.; Liu, H.-J.; Lo, H.-K.; Fedorov, A.; Copéret, C. An *N*-heterocyclic carbene ligand promotes highly selective alkyne semihydrogenation with copper nanoparticles supported on passivated silica. *Chem. Sci.* **2018**, *9*, 5366–5371. [\[CrossRef\]](#) [\[PubMed\]](#)
32. Imai, S.; Nakanishi, K.; Tanaka, A.; Kominami, H. Accelerated Semihydrogenation of Alkynes over a Copper/Palladium/Titanium (IV) Oxide Photocatalyst Free from Poison and H₂ Gas. *ChemCatChem* **2020**, *12*, 1609–1616. [\[CrossRef\]](#)
33. Gregori, B.J.; Schwarzhuber, F.; Pöllath, S.; Zweck, J.; Fritsch, L.; Schoch, R.; Bauer, M.; von Wangelin, A.J. Stereoselective Alkyne Hydrogenation by using a Simple Iron Catalyst. *ChemSusChem* **2019**, *12*, 3864–3870. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Shi, X.; Lin, Y.; Huang, L.; Sun, Z.; Yang, Y.; Zhou, X.; Vovk, E.; Liu, X.; Huang, X.; Sun, M.; et al. Copper Catalysts in Semihydrogenation of Acetylene: From Single Atoms to Nanoparticles. *ACS Catal.* **2020**, *10*, 3495–3504. [\[CrossRef\]](#)
35. García-Calvo, J.; Calvo-Gredilla, P.; Vallejos, S.; García, J.M.; Cuevas-Vicario, J.V.; García-Herbosa, G.; Avellab, M.; Torroba, T. Palladium nanodendrites uniformly deposited on the surface of polymers as an efficient and recyclable catalyst for direct drug modification via Z-selective semihydrogenation of alkynes. *Green Chem.* **2018**, *20*, 3875–3883. [\[CrossRef\]](#)
36. Lu, Y.; Feng, X.; Takale, B.S.; Yamamoto, Y.; Zhang, W.; Bao, M. Highly Selective Semihydrogenation of Alkynes to Alkenes by Using an Unsupported Nanoporous Palladium Catalyst: No Leaching of Palladium into the Reaction Mixture. *ACS Catal.* **2017**, *7*, 8296–8303. [\[CrossRef\]](#)
37. Fukazawa, A.; Minoshima, J.; Tanaka, K.; Hashimoto, Y.; Kobori, Y.; Sato, Y.; Atobe, M. A New Approach to Stereoselective Electrocatalytic Semihydrogenation of Alkynes to Z-Alkenes using a Proton-Exchange Membrane Reactor. *ACS Sustain. Chem. Eng.* **2019**, *7*, 11050–11055. [\[CrossRef\]](#)
38. Desai, S.P.; Ye, J.; Islamoglu, T.; Farha, O.K.; Lu, C.C. Mechanistic Study on the Origin of the *Trans* Selectivity in Alkyne Semihydrogenation by a Heterobimetallic Rhodium–Gallium Catalyst in a Metal–Organic Framework. *Organometallics* **2019**, *38*, 3466–3473. [\[CrossRef\]](#)
39. Long, Y.; Li, J.; Wu, L.; Wang, Q.; Liu, Y.; Wang, X.; Song, S.; Zhang, H. Construction of trace silver modified core@shell structured Pt–Ni nanoframe@CeO₂ for semihydrogenation of phenylacetylene. *Nano Res.* **2019**, *12*, 869–875. [\[CrossRef\]](#)
40. Yang, L.; Yu, S.; Peng, C.; Fang, X.; Cheng, Z.; Zhou, Z. Semihydrogenation of phenylacetylene over nonprecious Ni-based catalysts supported on AlSBA-15. *J. Catal.* **2019**, *370*, 310–320. [\[CrossRef\]](#)
41. Lomelí-Rosales, D.A.; Delgado, J.A.; de los Bernardos, M.D.M.; Pérez-Rodríguez, S.; Gual, A.; Claver, C.; Godard, C. A General One-Pot Methodology for the Preparation of Mono- and Bimetallic Nanoparticles Supported on Carbon Nanotubes: Application in the Semi-hydrogenation of Alkynes and Acetylene. *Chem. Eur. J.* **2019**, *25*, 8321–8331. [\[CrossRef\]](#) [\[PubMed\]](#)
42. Dang-Bao, T.; Pradel, C.; Favier, I.; Gómez, M. Bimetallic Nanocatalysts in Glycerol for Applications in Controlled Synthesis. A Structure–Reactivity Relationship Study. *ACS Appl. Nano Mater.* **2019**, *2*, 1033–1044. [\[CrossRef\]](#)
43. da Silva, F.P.; Fiorio, J.L.; Gonçalves, R.V.; Teixeira-Neto, E.; Rossi, L.M. Synergic Effect of Copper and Palladium for Selective Hydrogenation of Alkynes. *Ind. Eng. Chem. Res.* **2018**, *57*, 16209–16216. [\[CrossRef\]](#)
44. Desai, S.P.; Ye, J.; Zheng, J.; Ferrandon, M.S.; Webber, T.E.; Platero-Prats, A.E.; Duan, J.; Garcia-Holley, P.; Camaioni, D.M.; Chapman, K.W.; et al. Well-Defined Rhodium–Gallium Catalytic Sites in a Metal–Organic Framework: Promoter-Controlled Selectivity in Alkyne Semihydrogenation to *E*-Alkenes. *J. Am. Chem. Soc.* **2018**, *140*, 15309–15318. [\[CrossRef\]](#) [\[PubMed\]](#)
45. Wissing, M.; Niehues, M.; Ravoo, B.J.; Studer, A. Mixed AuPd Nanoparticles as Highly Active Catalysts for Alkyne Z-Semihydrogenation. *Eur. J. Org. Chem.* **2018**, *2018*, 3403–3409. [\[CrossRef\]](#)
46. Delgado, J.A.; Benkirane, O.; Claver, C.; Curulla-Ferré, D.; Godard, C. Advances in the preparation of highly selective nanocatalysts for the semi-hydrogenation of alkynes using colloidal approaches. *Dalton Trans.* **2017**, *46*, 12381–12403. [\[CrossRef\]](#) [\[PubMed\]](#)
47. Reina, A.; Favier, I.; Pradel, C.; Gómez, M. Stable Zero-Valent Nickel Nanoparticles in Glycerol: Synthesis and Applications in Selective Hydrogenations. *Adv. Synth. Catal.* **2018**, *360*, 3544–3552. [\[CrossRef\]](#)
48. Mäsing, F.; Nüsse, H.; Klingauf, J.; Studer, A. Light Mediated Preparation of Palladium Nanoparticles as Catalysts for Alkyne *cis*-Semihydrogenation. *Org. Lett.* **2017**, *19*, 2658–2661. [\[CrossRef\]](#) [\[PubMed\]](#)
49. Verho, O.; Zheng, H.; Gustafson, K.P.J.; Nagendiran, A.; Zou, X.; Bäckvall, J.-E. Application of Pd Nanoparticles Supported on Mesoporous Hollow Silica Nanospheres for the Efficient and Selective Semihydrogenation of Alkynes. *ChemCatChem* **2016**, *8*, 773–778. [\[CrossRef\]](#)
50. Sajiki, H.; Mori, S.; Ohkubo, T.; Ikawa, T.; Kume, A.; Maegawa, T.; Monguchi, Y. Partial Hydrogenation of Alkynes to *cis*-Olefins by Using a Novel Pd⁰–Polyethyleneimine Catalyst. *Chem. Eur. J.* **2008**, *14*, 5109–5111. [\[CrossRef\]](#)
51. Mori, S.; Ohkubo, T.; Ikawa, T.; Kume, A.; Maegawa, T.; Monguchi, Y.; Sajiki, H. Pd(0)–polyethyleneimine complex as a partial hydrogenation catalyst of alkynes to alkenes. *J. Mol. Catal. A* **2009**, *307*, 77–87. [\[CrossRef\]](#)
52. Yabe, Y.; Yamada, T.; Nagata, S.; Sawama, Y.; Monguchi, Y.; Sajiki, H. Development of a Palladium on Boron Nitride Catalyst and its Application to the Semihydrogenation of Alkynes. *Adv. Synth. Catal.* **2012**, *354*, 1264–1268. [\[CrossRef\]](#)

53. Yabe, Y.; Sawama, Y.; Yamada, T.; Nagata, S.; Monguchi, Y.; Sajiki, H. Easily-Controlled Chemoselective Hydrogenation by using Palladium on Boron Nitride. *ChemCatChem* **2013**, *5*, 2360–2366. [\[CrossRef\]](#)
54. Sajiki, H.; Hattori, K.; Hirota, K. Pd/C(en)-catalyzed regioselective hydrogenolysis of terminal epoxides to secondary alcohols. *Chem. Commun.* **1999**, 1041–1042. [\[CrossRef\]](#)
55. Sajiki, H.; Hattori, K.; Hirota, K. Easy and partial hydrogenation of aromatic carbonyls to benzyl alcohols using Pd/C(en)-catalyst. *J. Chem. Soc. Perkin Trans.* **1998**, *1*, 4043–4044. [\[CrossRef\]](#)
56. Sajiki, H.; Hattori, K.; Hirota, K. The Formation of a Novel Pd/C–Ethylenediamine Complex Catalyst: Chemoselective Hydrogenation without Deprotection of the O-Benzyl and N-Cbz Groups. *J. Org. Chem.* **1998**, *63*, 7990–7992. [\[CrossRef\]](#)
57. Hattori, K.; Sajiki, H.; Hirota, K. Undesirable deprotection of O-TBDMS groups by Pd/C-catalyzed hydrogenation and chemoselective hydrogenation using a Pd/C(en) catalyst. *Tetrahedron* **2001**, *57*, 2109–2114. [\[CrossRef\]](#)
58. Hattori, K.; Sajiki, H.; Hirota, K. Chemoselective control of hydrogenation among aromatic carbonyl and benzyl alcohol derivatives using Pd/C(en) catalyst. *Tetrahedron* **2001**, *57*, 4817–4824. [\[CrossRef\]](#)
59. Hattori, K.; Sajiki, H.; Hirota, K. The undesirable lability of tert-butyldimethylsilyl ethers under Pd/C-catalyzed hydrogenation conditions and solution of the problem by using a Pd/C(en) catalyst. *Tetrahedron Lett.* **2000**, *41*, 5711–5714. [\[CrossRef\]](#)
60. Hattori, K.; Sajiki, H.; Hirota, K. Pd/C(en)-catalyzed chemoselective hydrogenation with retention of the N-Cbz protective group and its scope and limitations. *Tetrahedron* **2000**, *56*, 8433–8441. [\[CrossRef\]](#)
61. Xia, L.; Li, D.; Long, J.; Huang, F.; Yang, L.; Guo, Y.; Jia, Z.; Xiao, J.; Liu, H. N-doped graphene confined Pt nanoparticles for efficient semi-hydrogenation of phenylacetylene. *Carbon* **2019**, *145*, 47–52. [\[CrossRef\]](#)
62. Li, X.; Pan, Y.; Yi, H.; Hu, J.; Yang, D.; Lv, F.; Li, W.; Zhou, J.; Wu, X.; Lei, A.; et al. Mott–Schottky Effect Leads to Alkyne Semihydrogenation over Pd-Nanocube@N-Doped Carbon. *ACS Catal.* **2019**, *9*, 4632–4641. [\[CrossRef\]](#)
63. Ji, G.; Duan, Y.; Zhang, S.; Fei, B.; Chen, X.; Yang, Y. Selective Semihydrogenation of Alkynes Catalyzed by Pd Nanoparticles Immobilized on Heteroatom-Doped Hierarchical Porous Carbon Derived from Bamboo Shoots. *ChemSusChem* **2017**, *10*, 3427–3434. [\[CrossRef\]](#) [\[PubMed\]](#)
64. Chen, F.; Kreyenschulte, C.; Radnik, J.; Lund, H.; Surkus, A.-E.; Junge, K.; Beller, M. Selective Semihydrogenation of Alkynes with N-Graphitic-Modified Cobalt Nanoparticles Supported on Silica. *ACS Catal.* **2017**, *7*, 1526–1532. [\[CrossRef\]](#)
65. Yoshii, T.; Umemoto, D.; Kuwahara, Y.; Mori, K.; Yamashita, H. Engineering of Surface Environment of Pd Nanoparticle Catalysts on Carbon Support with Pyrene–Thiol Ligands for Semihydrogenation of Alkynes. *ACS Appl. Mater. Interfaces* **2019**, *11*, 37708–37719. [\[CrossRef\]](#) [\[PubMed\]](#)
66. Zhang, Y.; Wen, X.; Shi, Y.; Yue, R.; Bai, L.; Liu, Q.; Ba, X. Sulfur-Containing Polymer As a Platform for Synthesis of Size-Controlled Pd Nanoparticles for Selective Semihydrogenation of Alkynes. *Ind. Eng. Chem. Res.* **2019**, *58*, 1142–1149. [\[CrossRef\]](#)
67. Zhao, X.; Zhou, L.; Zhang, W.; Hu, C.; Dai, L.; Ren, L.; Wu, B.; Fu, G.; Zheng, N. Thiol Treatment Creates Selective Palladium Catalysts for Semihydrogenation of Internal Alkynes. *Chem* **2018**, *4*, 1080–1091. [\[CrossRef\]](#)
68. Mori, A.; Mizusaki, T.; Kawase, M.; Maegawa, T.; Monguchi, Y.; Takao, S.; Takagi, Y.; Sajiki, H. Novel Palladium-on-Carbon/Diphenyl Sulfide Complex for Chemoselective Hydrogenation: Preparation, Characterization, and Application. *Adv. Synth. Catal.* **2008**, *350*, 406–410. [\[CrossRef\]](#)
69. Mori, A.; Miyakawa, Y.; Ohashi, E.; Haga, T.; Maegawa, T.; Sajiki, H. Pd/C-Catalyzed Chemoselective Hydrogenation in the Presence of Diphenylsulfide. *Org. Lett.* **2006**, *8*, 3279–3281. [\[CrossRef\]](#)
70. Yabe, Y.; Sawama, Y.; Monguchi, Y.; Sajiki, H. New aspect of chemoselective hydrogenation utilizing heterogeneous palladium catalysts supported by nitrogen- and oxygen-containing macromolecules. *Catal. Sci. Technol.* **2014**, *4*, 260–271. [\[CrossRef\]](#)
71. Monguchi, Y.; Ichikawa, T.; Sajiki, H. Recent Development of Palladium-supported Catalysts for Chemoselective Hydrogenation. *Chem. Pharm. Bull.* **2017**, *65*, 2–9. [\[CrossRef\]](#)
72. Guo, Z.; Liu, Y.; Liu, Y.; Chu, W. Promising SiC support for Pd catalyst in selective hydrogenation of acetylene to ethylene. *Appl. Surf. Sci.* **2018**, *442*, 736–741. [\[CrossRef\]](#)
73. Ichikawa, T.; Netsu, M.; Mizuno, M.; Mizusaki, T.; Takagi, Y.; Sawama, Y.; Monguchi, Y.; Sajiki, H. Development of a Unique Heterogeneous Palladium Catalyst for the Suzuki–Miyaura Reaction using (Hetero)aryl Chlorides and Chemoselective Hydrogenation. *Adv. Synth. Catal.* **2017**, *359*, 2269–2279. [\[CrossRef\]](#)
74. Ding, Z.; Li, C.; Chen, J.; Zeng, J.; Tang, H.; Ding, Y.; Zhan, Z. Palladium/Phosphorus-Doped Porous Organic Polymer as Recyclable Chemoselective and Efficient Hydrogenation Catalyst under Ambient Conditions. *Adv. Synth. Catal.* **2017**, *359*, 2280–2287. [\[CrossRef\]](#)
75. Qi, H.L.; Chen, D.S.; Ye, J.S.; Hung, J.M. Electrochemical Technique and Copper-Promoted Transformations: Selective Hydroxylation and Amination of Arylboronic Acids. *J. Org. Chem.* **2013**, *78*, 7482–7487. [\[CrossRef\]](#) [\[PubMed\]](#)
76. Das, B.G.; Ghorai, P. The direct reductive amination of electron-deficient amines with aldehydes: The unique reactivity of the Re₂O₇ catalyst. *Chem. Commun. Chem.* **2012**, *48*, 8276–8278. [\[CrossRef\]](#) [\[PubMed\]](#)
77. Shen, D.; Miao, C.; Xu, D.; Xia, C.; Sun, W. Highly Efficient Oxidation of Secondary Alcohols to Ketones Catalyzed by Manganese Complexes of N₄ Ligands with H₂O₂. *Org. Lett.* **2015**, *17*, 54–57. [\[CrossRef\]](#) [\[PubMed\]](#)
78. Chen, Y.; Li, C.; Cui, Y.; Sun, M.; Jia, X.; Li, J. Bu₄Ni-Catalyzed C–C Bond Cleavage and Oxidative Esterification of Allyl Alcohols with Toluene Derivatives. *Synthesis* **2019**, *51*, 3667–3674. [\[CrossRef\]](#)
79. Mao, R.; Balon, J.; Hu, X. Decarboxylative C(sp³)–O Cross-Coupling. *Angew. Chem. Int. Ed.* **2018**, *57*, 13624–13628. [\[CrossRef\]](#) [\[PubMed\]](#)

80. Malapit, C.A.; Ichiishi, N.; Sanford, M.S. Pd-Catalyzed Decarbonylative Cross-Couplings of Aryl Chlorides. *Org. Lett.* **2017**, *19*, 4142–4145. [[CrossRef](#)] [[PubMed](#)]
81. Sloan, M.E.; Staubitz, A.; Lee, K.; Manners, I. Scope and Selectivity of Heterogeneous Rh⁰-Catalyzed Tandem Dehydrocoupling/Hydrogenation Using Me₂NH·BH₃ as a Stoichiometric H₂ Source. *Eur. J. Org. Chem.* **2011**, *2011*, 672–675. [[CrossRef](#)]
82. Wang, Y.; Cao, X.; Zhao, L.; Pi, C.; Ji, J.; Cui, X.; Wu, Y. Generalized Chemoselective Transfer Hydrogenation/Hydrodeuteration. *Adv. Synth. Catal.* **2020**, *362*, 4119–4129. [[CrossRef](#)]
83. Richmond, E.; Moran, J. Ligand Control of *E/Z* Selectivity in Nickel-Catalyzed Transfer Hydrogenative Alkyne Semireduction. *J. Org. Chem.* **2015**, *80*, 6922–6929. [[CrossRef](#)] [[PubMed](#)]
84. Ho, G.; Judkele, L.; Bruffaerts, J.; Marek, I. Metal-Catalyzed Remote Functionalization of ω -Ene Unsaturated Ethers: Towards Functionalized Vinyl Species. *Angew. Chem. Int. Ed.* **2018**, *57*, 8012–8016. [[CrossRef](#)]
85. Broggi, J.; Jurčík, V.; Songis, O.; Poater, A.; Cavallo, L.; Slawin, A.M.Z.; Cazin, C.S.J. The Isolation of [Pd{OC(O)H}(H)(NHC)(PR₃)] (NHC = N-Heterocyclic Carbene) and Its Role in Alkene and Alkyne Reductions Using Formic Acid. *J. Am. Chem. Soc.* **2013**, *135*, 4588–4591. [[CrossRef](#)] [[PubMed](#)]
86. Moon, S.; Kim, U.; Sung, D.; Kim, W. A Synthetic Approach to *N*-Aryl Carbamates via Copper-Catalyzed Chan–Lam Coupling at Room Temperature. *J. Org. Chem.* **2015**, *80*, 1856–1865. [[CrossRef](#)]
87. Shen, G.; Liu, H.; Chen, J.; He, Z.; Zhou, Y.; Wang, L.; Luo, Y.; Su, Z.; Fan, B. Zinc salt-catalyzed reduction of α -aryl imino esters, diketones and phenylacetylenes with water as hydrogen source. *Org. Biomol. Chem.* **2021**, *19*, 3601–3610. [[CrossRef](#)] [[PubMed](#)]
88. Bhattacharjee, A.; Hosoya, H.; Ikeda, H.; Nishi, K.; Tsurugi, H.; Mashima, K. Metal-Free Deoxygenation and Reductive Disilylation of Nitroarenes by Organosilicon Reducing Reagents. *Chem. Eur. J.* **2018**, *24*, 11278–11282. [[CrossRef](#)] [[PubMed](#)]
89. Yang, C.; Han, J.; Liu, J.; Li, Y.; Zhang, F.; Yu, H.; Hu, S.; Wang, X. Pd-Catalyzed Vinylation of Aryl Halides with Inexpensive Organosilicon Reagents Under Mild Conditions. *Chem. Eur. J.* **2018**, *24*, 10324–10328. [[CrossRef](#)] [[PubMed](#)]