

Highly Reusable and Active Nanometal—Silicon-Nanowire Array Hybrid Catalysts for Hydrogenation

Heeyoel Baek,^[a] Takuma Sato,^[a] Yasuhiro Uozumi,^[b] and Yoichi M. A. Yamada*^[a]

Highly reusable and active silicon-nanowire-array-stabilized metal-nanoparticle (SiNA-MNP) catalysts are prepared for effective hydrogenation under mild conditions. Monometallic Pd (SiNA-Pd), platinum (SiNA-Pt), and rhodium (SiNA-Rh) nanoparticles are prepared on silicon nanowire arrays by the silvernanoparticle-assisted chemical etching of silicon wafers with a variety of metal precursors. Moreover, bimetallic Pd-Rh (SiNA-PdRh) and Pd-Pt (SiNA-PdPt) nanoalloy catalysts are also synthesized in one-pot processes in mixed-metal solutions without any reducing agent, such as NaBH₄ or H₂ gas, and other external factors. The SiNA-MNP catalysts were characterized by SEM/EDX, TEM, XAFS, XRD, and ICP-MS. Each catalyst was used to hydrogenate trans-stilbene in a 0.1 MPa hydrogen atmosphere to assess catalytic activity. Moreover, the SiNA-PdPt and SiNA-PdRh alloy catalysts are also robust and stable, with high reusability numbers for hydrogenation.

The catalytic hydrogenation of a carbon–carbon multiple bond is a useful and versatile chemical conversion in the fine chemicals, pharmaceuticals, and food industries.^[1] The hydrogenation reactions are carried out by molecular hydrogen in the presence of a Pt, Fe, Ni, Rh, Co, Ru, or Pd catalyst on a solid support, such as silica, activated carbon, or alumina.^[2,3] However, heterogeneous catalysts that are highly reusable and stable are still in demand. Discovering a simple and general catalyst that can facilitate catalytic hydrogenation under mild conditions remains a challenging but rewarding task.

To further improve their catalytic performance, catalysts are often modified in a variety of ways. Particularly, the bimetallization of a solid support not only provides unique reaction properties, such as electrical and alloy synergism, but also efficient catalytic activity.^[4] For example, among such bimetallic or alloy catalysts, SiO₂-supported Pd–Ni bimetallic catalysts have attracted significant attention due to their remarkable stabilities and high selectivities.^[5]

The conventional preparation of a heterogeneous metallic catalyst typically involves electrodeposition and the simulta-

[a]	Dr. H. Baek, Dr. T. Sato, Dr. Y. M. A. Yamada
	RIKEN Center for Sustainable Resource Science,
	351-0198 Wako, Saitama, Japan
	E-mail: ymayamada@riken.jp
[b]	Prof. Dr. Y. Uozumi
	Institute for Molecular Science (IMS),
	444-8787 Okazaki, Aichi, Japan
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neous or successive chemical reduction of one or two different metal precursors, which often requires the use of a reducing or stabilizing agent, such as NaBH₄, N₂H₂, H₂ gas, or a polymer (Figure 1a).^[6] It is worth noting that the selection of a suitable support material and the development of an appropriate preparation method can enhance the catalytic activity of supported metal nanoparticles.^[7]

Silicon nanowire arrays (SiNAs) can be used as nanostructure templates^[8] and as reducing agents suitable for the reductive formation of metal nanoparticles without the need for an additional reducing agent, such as $NaBH_4$ or H_2 gas, or other external factors (Figure 1b and Figure 1c). The hydrogenterminated surfaces of SiNA^[9] readily reduce metal ions, such as Pd, Ag, and Rh to metal aggregates of various morphologies on SiNA surfaces in solution at room temperature.^[10] We previously reported the preparation of monometallic SiNA-MNP (SiNA-Pd and SiNA-Rh) and its use in organic transformations, such as the Mizoroki-Heck reaction, C-H arylations, and carboxylic acid decarboxylations.^[11,12] In particular, SiNA-Pd was found to be highly reusable (over 150 times) during hydrogenation while maintaining its high activity. Moreover, we showed that the palladium nanoparticles were immobilized on the surface of the metallic silicon nanowire array through the formation of palladium silicide (PdSi). Since this metal-support interaction is very strong, this immobilization method, which involves metalsupported agglomeration, improves the stability and reusability of a heterogeneous catalyst, and resolves problems associated with metal leaching from the support.



Figure 1. Schematic images showing the preparation of solid-supported metal-nanoparticle catalysts.



Herein, we report the development of monometallic nanoparticle composites located in SiNA nanostructures. In addition, we developed a method for the preparation of durable bimetallic nanoparticle catalysts on SiNA using a facile one-pot metal-supported agglomeration process. All SiNA-MNPs catalyze the hydrogenation of *trans*-stilbene under mild conditions and can be reused many times without the loss of catalytic activity. At the same time, we investigated the structures of the Pd, Rh, and Pt species on the SiNAs by SEM/EDX, TEM, XAFS, and XRD.

Toward an additive-free approach devoid of reducing agents, we developed an alternative synthetic method that uses the hydrogen-terminated surface of SiNA. This strategy involves a simple one-pot process to prepare monometallic and bimetallic nanoparticle-SiNAs at room temperature. A schematic image of the experimental route used to prepare SiNA-MNPs is shown in Figure 2. Initially, SiNA is prepared by the silver-nanoparticle-assisted chemical etching of *a p*-type silicon wafer in a mixture of hydrofluoric acid and hydrogen peroxide. The metal nanoparticles are agglomerated into the SiNA through

the reduction of each metal ion on the SiNA surface bearing terminal hydrogens. Moreover, we also developed bimetallic catalysts containing palladium-platinum (PdPt) and palladium-rhodium (PdRh) nanoparticles. Bimetal-doped SiNA catalysts were prepared by a one-pot process under similar conditions in a mixture of metal precursors devoid of reducing agents, such as H_2 gas or NaBH₄, at room temperature.

The morphology of catalysts and the size of nanoparticles on SiNA were determined by using cross-sectional scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images of sections of SiNA-Pd (Figure 3a), SiNA-Pt (Figure 3d), and SiNA-Rh (Figure 3g) reveal nanowire lengths and widths of approximately $5-10 \,\mu$ m and below 900 nm, respectively. Dispersion of metal atoms over the catalyst surfaces was mapped with energy-dispersive X-ray (EDX), and showed that Pd (Figure 3b), Pt (Figure 3e), and Rh(Figure 3h) nanoparticles are located across the entire surface of their respective SiNAs.

The SEM images of bimetallic SiNA-PdPt (Figure 4a) and SiNA-PdRh (Figure 4e) also show similar well-defined nano-



Figure 2. A schematic image depicting the preparation of SiNA-MNP catalysts.



Figure 3. Cross-sectional SEM/EDX and TEM images of monometallic SiNA-MNP: (a-c) SiNA-Pd, (d-f) SiNA-Pt, and (g-i) SiNA-Rh.



Figure 4. Cross-sectional SEM/EDX images and TEM images of bimetallic SiNA-MNP catalysts: (a–d) SiNA-PdPt and (e–h) SiNA-PdRh.



structures, with the presence of bimetallic PdPt and PdRh nanoparticles on the SiNA surfaces confirmed by EDX images (Figure 4b, Figure 4c and Figure 4f, Figure 4g). The TEM images of SiNA-Pd, -Pt, and -Rh reveal dispersed Pd, Pt, and Rh nanoparticles with diameters of approximately 9–11 nm, 3–4 nm, and 4–5 nm, respectively (Figure 3c, Figure 3f, Figure 3i), while the TEM images of bimetallic SiNA-PdPt and SiNA-PdRh show dispersed nanoparticles with diameters of approximately 7–9 nm and 9–11 nm, respectively (Figure 4d and Figure 4h).

To investigate the chemical states of the nanoparticles, monometallic SiNA-Pd and SiNA-Rh, as well as bimetallic SiNA-PdRh, were subjected to XAFS experiments at the Pd K-edge (24.4 keV) and Rh K-edge (23.2 keV). By comparison with Pd and Rh foil as reference materials, the XANES spectral features of the catalyst samples on Pd (Figure 5a) and Rh (Figure 5d) clearly reveal that both Pd and Rh are in their metallic zero-valence oxidation states, while the catalyst samples show reduction in extended X-Ray absorption fine structure (EXAFS) intensity in *k*-space (Figure 5b (Pd) and Figure 5e (Rh)) and *R*-space (Figure 5c (Pd) and 5f (Rh)), which strongly suggests that metallic Pd and Rh nanoparticles are formed on the surface of the silicon nanowire array through chemical reduction by the hydrogenterminated silicon surface. Furthermore, the Rh K-edge EXAFS



Figure 5. XAFS data for SiNA-Pd, SiNA-Rh, and SiNA-PdRh. (a) Pd K-edge XANES, (b) Pd K-edge EXAFS in *k*-space, (c) Pd K-edge EXAFS in *R*-space, (d) Rh K-edge XANES, (e) Rh K-edge EXAFS in *k*-space, (f) Rh K-edge in *R*-space (*k*-range: 3–15 Å⁻¹).

Table 1. EXAFS fitting data. ^[a]							
Sample	Edge	N ^[b]	R [Å] ^[c]	σ2 [Å2]	R factor		
Pd foil SiNA-Pd ^[e] SiNA-PdRh ^[e,f] Rh foil SiNA-Rh ^[e] SiNA-PdRh ^[e,f]	Pd-K Pd-K Pd-K Rh-K Rh-K Rh-K	12 ^{[d}] 8.8(4) 7.9(5) 12 ^[d] 7.3(5) 8.4(8)	2.742(3) 2.740(2) 2.739(2) 2.689(2) 2.685(3) 2.700(4)	0.006 0.006 0.007 0.005 0.006 0.007	0.002 0.001 0.002 0.002 0.002 0.004		

[a] *k*-Range: 3–15 Å⁻¹, *R*-range: 1.9–2.8 Å. S_0^{-2} is assumed to be 1. All spectra were acquired at room temperature. [b] Mean coordination number of the first coordination shell. [c] Pd(Rh)–Pd(Rh) distance. [d] The coordination number of the bulk-metal foil is assumed to be 12. [e] Acquired in fluorescence mode. [f] The ratio of Rh:Pd is ~1:3, based on ICP-MS.

spectrum of bimetallic SiNA-PdRh in *R*-space (Figure 5f) suggests that the Rh– metal bond is elongated compared to those in Rh foil and monometallic SiNA-Rh, which indicates the existence of Pd–Rh solid-solution alloy nanoparticles. The fitted data for the first coordination shell in *R*-space (1.9–2.8 Å) are summarized in Table 1, which shows that the mean coordination number of each metal (Pd or Rh) in each catalyst sample (SiNA-Pd, -Rh, or -PdRh) is lower than that of the face-centered cubic-packed bulk metal (7.3–8.8 vs. 12). Most importantly, the Rh–M (M=Pd, Rh (3:1)) bond in SiNA-PdRh is clearly longer (2.700 Å) than that in Rh foil (2.689 Å). XPS revealed that the Pt 4f_{7/2} binding energy of SiNA-PdPt (70.3 eV) is negatively shifted compared to that of monometallic SiNA-Pt (70.5 eV), suggesting charge transfer from Pd atoms to Pt atoms (Figure S1, Supporting Information).^[13]

Since distinguishing atomic species with close atomic numbers (45Rh and 46Pd) is difficult by EXAFS, the structures and phase information of the metallic nanoparticles were further investigated by XRD (Figure 6). Pd nanoparticles on SiNA exhibit diffraction peaks at around 40.1° and 46.6° that are assigned to the (111) and (200) planes, respectively, of the face-centered cubic structure (fcc) of Pd (Figure 6, deep-green trace; PDF 00-0046-1043). The diffraction peak at 41.1° of the Rh nanoparticles are assigned to the (111) crystalline plane of metallic Rh (Figure 6, green trace; PDF 00-005-0685). Similarly, the main (111) reflection of the formed PdRh is shifted along the 2θ axis to 40.2°, and lies between the limits of pure Pd and Rh, consistent with the formation of the PdRh alloy (Figure 6, red trace).^[14] The diffractin peaks of PdPt bimetallic nanoparticles on SiNA are observed between the limits of pure Pd and Pt (Figure S3, Supporting Information)^[15]. In addition, the remaining intense reflections are ascribed to the silicon nanowire array and the silicon substrate, which is due to the introduction of the silicon wafer as the catalyst support. These data provide evidence for the formation of PdRh and PdPt alloys.

We used ICP-MS to determine the nanoparticle loading on SiNA, which revealed contents of 14.0 μ mol/g, 6.07 μ mol/g, and 4.32 μ mol/g on SiNA-Pd, -Pt, and -Rh, respectively. The actual ratio between metals contents in bimetallic SiNA-PdPt and



Figure 6. XRD patterns of monometallic Pd, Rh, and bimetallic PdRh on SiNA.



-PdRh are 0.65:0.35 (11.2 $\mu mol/g$ Pd+5.97 $\mu mol/g$ Pt) and 0.81:0.19 (8.55 $\mu mol/g$ Pd+1.996 $\mu mol/g$ Rh).

The catalytic performance of the SiNA-Pd, -Pt, -Rh, -PdPt, and -PdRh catalysts was evaluated by hydrogenating *trans*stilbene (1) to bibenzyl (2) in EtOH at 70 °C. The monometallic SiNA-Pd and -Rh catalysts gave 2 in yields of up to 99%, while the SiNA-Pt catalyst showed lower catalytic activity (70% yield after 24 h). The bimetallic SiNA-PdPt and -PdRh catalysts exhibited high catalytic activities over 24 h in 0.1 MPa of hydrogen gas to deliver yields of 99% (Scheme 1).

To further evaluate the catalytic performance of the catalysts, they were subjected to reusability testing under similar conditions to those described above. Monometallic SiNA-Pd showed high hydrogenation activity (Figure 7); however, SiNA-Pt showed poor reusability with yields of 63% (2nd use) and 51% (3rd use). In addition, the SiNA-Rh catalyst also



Scheme 1. Hydrogenation of *trans*-stilbene with SiNA-MNP catalysts.



Figure 7. Reusability testing of the SiNA-MNP catalysts.

gave bibenzyl in 95% (2nd use) and 55% yield (3rd use), with significant loss of catalytic activity. On the other hand, both bimetallic catalysts (SiNA-PdRh and -PdPt) exhibited no significant loss of catalytic activity and were reusable over 50 times with persistent catalyst activity observed (Figure 7). Cumulative turnover numbers (TONs) were calculated by normalizing bibenzyl conversion; the TONs of the catalysts are 29,100 (based on total PdPt nanoparticle) and 12,375 (based on total PdRh nanoparticle), respectively. The bimetallic nanoalloy catalysts (SiNA-PdRh and -PdPt) were more durable and exhibited greater catalytic activity when Pd was present, with higher reusability numbers and significantly improved stabilities observed.

In summary, we successfully prepared monometallic SiNA-Pd, SiNA-Rh, and SiNA-Pt catalysts by the confined metal etching of silicon nanowire arrays with Ag nanoparticles. Moreover, PdRh and PdPt alloy catalysts were also synthesized on SiNA through a simple one-pot process in mixed-metal solutions without any external factors. The prepared catalysts were used to catalytically hydrogenate trans-stilbene under hydrogen and then reused. SiNA-Pd and the SiNA-PdPt and SiNA-PdRh nanoalloy catalysts were catalytically stable compared to the other monometallic catalysts (SiNA-Pt and -Rh). Moreover, they were reused more than 50 times without significant loss of catalytic activity. The method described herein provides a simple approach to the synthesis of highly stable and robust alloy or monometallic catalysts on silicon supports; we believe that it will be useful when designing new powerful catalytic systems for green and sustainable organic reaction applications.

Experimental Section

Catalytic hydrogenation with the SiNA-MNP catalysts

Each SiNA-MNP catalyst (0.0006 mmol Pd, 0.0006 mmol Pt, 0.0005 mmol Rh, 0.0006 mmol PdRh, or 0.00085 mmol PdPt) and *trans*-stilbene (0.5 mmol) in ethanol (2 mL) were added to a 10-mL glass vessel and stirred under H₂ (0.1 MPa, balloon) at 70 °C for 24 h using a vortex mixer with a temperature controller. After cooling to room temperature, the reaction mixture was analyzed by GC (HP-1) with dodecane as the internal standard to determine the yield. The catalyst was easily recovered using tweezers, washed with ethanol, acetone, and H₂O, and then dried under a flow of N₂ for the next reaction.

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Conflict of Interest

The authors declare no conflict of interest.

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- [1] a) S. Nishimura, Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis, Wiley, New York, 2001; b) P. N. Rylander, Hydrogenation Methods, Academic Pres, New York, 1985; c) M. Besson, P. Gallezot, C. Pinel, Chem. Rev. 2014, 114, 1827–1870.
- [2] a) W. Yu, M. D. Porosoff, J. G. Chen, Chem. Rev. 2012, 112, 5780–5817;
 b) R. Yun, S. Zhang, W. Ma, X. Lv, S. Liu, T. Sheng, S. Wang, Inorg. Chem.
 2019, 58, 9469–9475; c) E. A. Karakanov, A. V. Zolotukhina, A. O. Ivanov,
 A. L. Maximov, Chem. Open 2019, 8, 358–381; d) Y. Niu, L. K. Yeung,
 R. M. Crooks, J. Am. Chem. Soc. 2001, 123, 6840–6846; e) H. Yoshida, Y.
 Onodera, S. Fujita, H. Kawamori, M. Arai, Green Chem. 2015, 17, 1877–1883; f) J. Wang, Y. Wang, G. Chen, Z. He, Catalysis 2018, 8, 309.
- [3] a) P. Ryachuk, G. Agostini, M.-M. Pohl, H. Lund, A. Agapova, H. Junge, K. Junge, M. Beller, *Sci. Adv.* 2018, *4*, 1–10; b) H. Liu, T. Jiamg, B. Han, S. Liang, Y. Zhou, *Science* 2009, *326*, 1250–1252; c) D. D. Das, A. Sayari, *J. Catal.* 2007, *246*, 60–65; d) Z. Chen, W. Wang, Y. Zhang, Y. Liang, Z. Cui, X. Wang, *Langmuir* 2018, *34*, 12809–12814; e) S. Banerjee, V. Balasanthiran, R. T. Koodali, G. A. Sereda, *Org. Biomol. Chem.* 2010, *8*, 4316–4321.
- [4] a) M. Sankar, N. Dimitratos, P. J. Miedziak, P. P. Wells, C. J. Kiely, G. J. Hutcings, *Chem. Soc. Rev.* 2012, *41*, 8099–8139; b) G. Zhang, C. Huang, R. Qin, Z. Shao, D. An, W. Zhang, Y. Wang, *J. Mater. Chem. A* 2015, *3*, 5204–5211; c) S. Furukawa, T. Komatsu, *ACS Catal.* 2017, *7*, 735–765; d) Z. Xu, Y. Zhu, L. Bai, Q. Lang, W. Hu, C. Gao, S. Zhong, S. Bai, *Inorg.*

Chem. Front. 2017, 4, 1704–1713; e) K. A. Goulas, S. Sreekumar, Y. Song, P. Kharidehal, G. Gunbas, P. J. Dietrich, G. R. Johnson, Y. C. Wang, A. M. Grippo, L. C. Grabow, A. A. Gokhale, F. D. Toste, J. Am. Chem. Soc. 2016, 138, 6805–6812.

- [5] a) X. Wang, X. Liang, P. Geng, Q. Li, ACS Catal. 2020, 10, 2395–2412;
 b) H. Liu, K. Tao, C. Xiong, S. Zhou, Catal. Sci. Technol. 2015, 5, 405–414.
- [6] a) C. E. D. Chidsey, D. N. Loiacono, *Langmuir* **1990**, *6*, 682–691; b) Y. Ren,
 Y. Wang, X. Li, Z. Zhang, Q. Chi, *New J. Chem.* **2018**, *42*, 16694–16702;
 c) K.-W. Wang, Z. Yu, A. Hu, Y.-Y. Hsu, T. L. Chen, C.-Y. Lin, C.-W. Hu, Y.-T.
 Yang, T.-Y. Chen, *RSC Adv.* **2017**, *7*, 55110–55120; d) Z. Li, Y. Chen, G. Fu,
 Y. Chen, D. Sun, J.-M. Lee, Y. Tang, *Nanoscale* **2019**, *11*, 2974–2980.
- [7] L. L. Chng, N. Erathodiyil, J. Y. Ying, Acc. Chem. Res. 2013, 46, 1825–1837.
- [8] a) T. K. Sham, I. Coulthard, J. W. Lorimer, A. Hiraya, M. Watanabe, *Chem. Mater.* 1994, *6*, 2085–2091; b) I. Coulthard, T. K. Sham, *Solid State Commun.* 1998, *105*, 751–754.
- [9] a) G. W. Trucks, K. Raghavachari, G. S. Higashi, Y. J. Chabal, *Phy. Rev. Lett.* 1990, *65*, 504–507; b) V. Schmidt, J. V. Wittemann, U. Gösele, *Chem. Rev.* 2010, *110*, 361–388.
- [10] X.-H. Sun, N.-B. Wong, C.-P. Li, S.-T. Lee, P.-S. Kim, T.-K. Sham, Chem. Mater. 2004, 16, 1143–1152.
- [11] a) Y. M. A. Yamada, Y. Yuyama, T. Sato, S. Fujikawa, Y. Uozumi, Angew. Chem. Int. Ed. 2014, 53, 127–131; Angew. Chem. 2014, 126, 131–135;
 b) Y. M. A. Yamada, H. Baek, T. Sato, A. Nakao, Y. Uozumi, Commun. Chem. 2020, 3, 81.
- [12] H. Baek, K. Kashimura, T. Fujii, S. Tsubaki, Y. Wada, S. Fujikawa, T. Sato, Y. Uozumi, Y. M. A. Yamada, ACS Catal. 2020, 10, 2148–2156.
- [13] G. Zhang, C. Huang, R. Qin, Z. Shao, D. An, W. Zhang, Y. Wang, J. Mater. Chem. A 2015, 3, 5204–5211.
- [14] P. J. Cappillino, J. D. Sugar, M. A. Hekmaty, B. W. Jacobs, V. Stavila, P. G. Kotula, J. M. Chames, N. Y. Yang, D. B. Robinson, *J. Mater. Chem.* 2012, 22, 14013–14022.
- [15] Y.-W. Lee, A.-Ra. Ko, S.-B. Han, H.-S. Kim, K.-W. Park, Phys. Chem. Chem. Phys. 2011, 13, 5569–5572.

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