

Chemoselective hydrogenation of heteroarenes and arenes by Pd-Ru-PVP under mild reaction conditions

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Experimental Section

General

All chemicals were obtained from Tokyo Chemical Industry and Wako Pure Chemical Industries, Japan and were used without further purification.

Catalyst preparation

i) Wet chemical reduction method

Polyvinylpyrrolidone (PVP)-stabilized monometallic (Pd, Ru) and bimetallic (Pd_{0.5}-Ru_{0.5}) catalysts were prepared by using a wet reduction method.^{S1} In a typical procedure, an appropriate amount of metal chloride precursor (1 equivalent) was dissolved in deionized water. Five equivalents of PVP were added to ethylene glycol, and the mixture was heated to 200 °C. An aqueous solution of metal precursor was added slowly to the ethylene glycol at 200 °C. After the addition was complete, the temperature of the mixture was maintained for 30 min, and then the mixture was cooled to room temperature. The prepared nanoparticles were separated by centrifuging. The bimetallic (Pd_{0.5}-Ru_{0.5}) catalyst was prepared by controlling the molar ratio of Pd²⁺ and Ru³⁺ ions.

ii) Microwave-assisted, wet chemical reduction method

In a standard procedure, metal chloride (1 equivalent) and PVP (5 equivalents) were dissolved in ethylene glycol.^{S2} After purging with Ar, the vessel was sealed and heated to 180 °C by microwave irradiation (400 W) for 15 min. The resultant black suspension was separated by centrifuging.

Table S1. Preparation procedure of various metal NPs

Metal (M)	Preparation method	M-PVP ^a (%)
Pd	Wet chemical reduction	29
Ru	Wet chemical reduction	55
Pd-Ru	Wet chemical reduction	40
Rh	Micro-wave assisted wet chemical reduction	82

^aCalculated by thermogravimetric analysis

Catalyst characterization

High-angle, annular, dark-field scanning transmission electron microscopy images and elemental mappings via energy-dispersive X-ray analysis were obtained on a JEM-ARM200F electron microscope (JEOL, Japan) operated at 120 kV. X-ray photoelectron spectroscopy analysis was carried out using an ESCA-3400 (Shimadzu, Kyoto, Japan). The PVP amount was estimated by using thermogravimetric analysis (ThermoPlus; Rigaku, Japan).

General procedure for the hydrogenation of heteroarenes and arenes

All reactions were carried out in a 10-mL autoclave using a glass tube and magnetic stirrer. In a standard run, substrate (1 mmol), solvent (1 mL), and catalyst (1.4 mol%) were added to the reactor. In the case of an arene substrate, no solvent was used. Next, the reactor was purged with H₂ gas multiple times, and the reactor was pressurized (5–10 bar). The reaction of heteroarenes was carried out at room temperature with constant stirring. For arenes, the reactor was heated to 150 °C with constant stirring. After completion of the reaction, the catalyst was separated with a syringe micro-filter. The conversion of substrate and yield of product were calculated using internal standards with a gas chromatograph (Shimadzu 2014) equipped with a flame-ionization detector.

Table S2. Comparison between reported results and the results with our catalytic methods for the hydrogenation of quinoline

Entry	Catalyst (mol %)	H ₂ (bar)	Temp. (°C)	Reaction time (h)	TOF (h ⁻¹)	Substrate scope	Ref.
1	CoCl ₂ (5)	NaBH ₄	130	17	1.1	<i>N</i> -heteroarenes	7
2	Au/HAS-TiO ₂ (1)	20	80	3.5	28.5	<i>N</i> -heteroarenes	8
3	Ru-SiO ₂ @mSiO ₂ (0.67)	30	90	5	29.8	<i>N</i> -heteroarenes	9
4	Ru-NPs in IL (2)	10	80	19	2.6	<i>N</i> -heteroarenes	10
5	Pd-pol (0.5)	10	80	9	22.2	<i>N</i> -heteroarenes	11
6	Pt (5)	H ₂ balloon	25	1.33	15	<i>N</i> -heteroarenes	12
7	Rh/AlO(OH) (1.5)	8	80	3	22.2		13
8	BWT _{1.5} -Rh (1)	20	80	0.5	200	<i>N</i> -heteroarenes	14
9	Rh NPs (1.8)	30	50	5	20	<i>N</i> -heteroarenes	15
10	PEG ₄₀₀₀ -Rh NPs (0.1)	30	100	6	323	<i>N</i> -heteroarenes	16
11	Rh NPs (1)	30	80	15	2.08	<i>N</i> -heteroarenes, <i>O</i> -heteroarenes	17
12	Rh@Fe ₂ O ₃ (0.9)	20	50	2	54	<i>N</i> -heteroarenes	18
13	NHC-Rh (0.62)	20	30		238	<i>N</i> -heteroarenes, arenes	19
14	Rh NP-rGO (1)	10	80	12	4.16	<i>N</i> -heteroarenes, <i>O</i> -heteroarenes	20
15	Rh-C60 (0.6)	20	100	4	164.3	<i>N</i> -heteroarenes	21
16	Rh/AlO(OH) (1)	1	25	6	3.1	<i>N</i> -heteroarenes, arenes	22
17	Rh/AlO(OH) (5)	1	22	6	9	<i>N</i> -heteroarenes, arenes	23
18	HEA16Cl-Rh (1)	1	25	10.4	10.9	<i>N</i> -heteroarenes, <i>O</i> -heteroarenes	24
19	Pd-Ru-PVP (2)	5	25	6	8.3	<i>N</i>-heteroarenes, <i>O</i>-heteroarene, arenes	This work

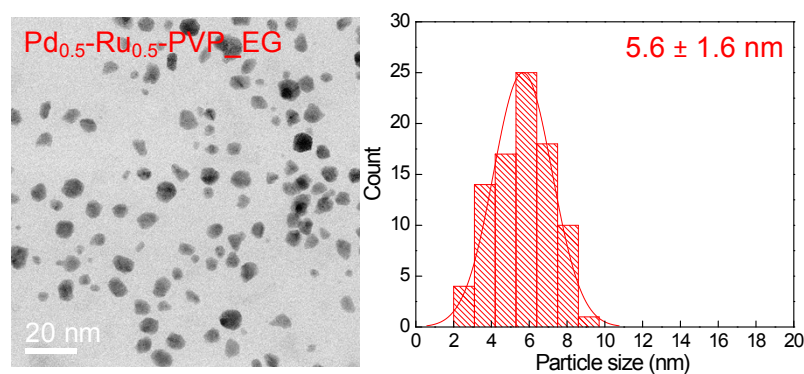


Figure S1. High-resolution STEM image and size distribution of the Pd_{0.5}Ru_{0.5}-PVP catalyst.

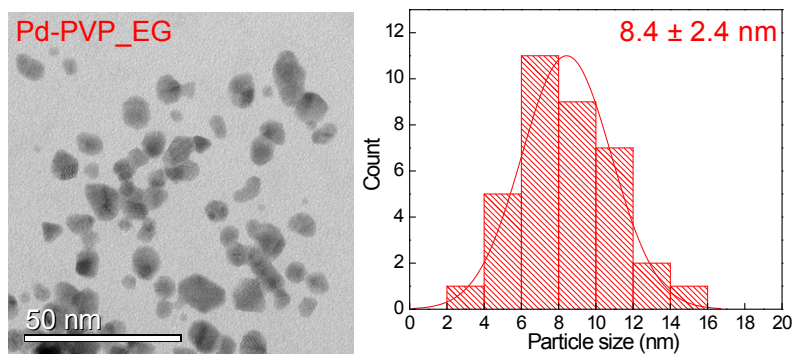


Figure S3. High-resolution STEM image and size distribution of the Pd-PVP catalyst.

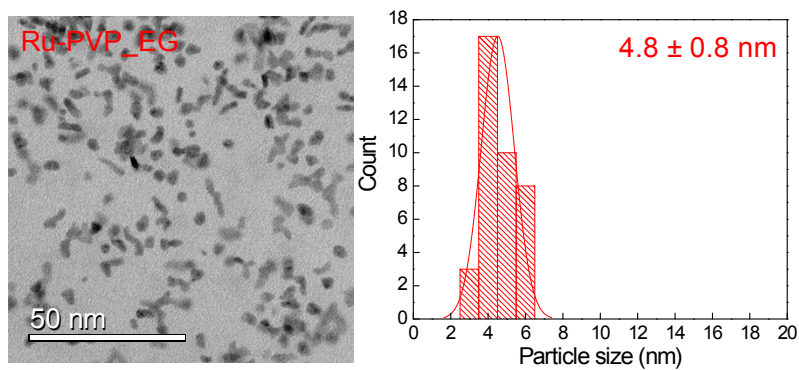


Figure S4. High-resolution STEM image and size distribution of the Ru-PVP catalyst.

References

- ^{S1}K. Kusada, H. Kobayashi, R. Ikeda, Y. Kubota, M. Takata, S. Toh, T. Yamamoto, S. Matsumura, N. Sumi, K. Sato, K. Nagaoka and H. Kitagawa, *J. Am. Chem. Soc.*, 2014, **136**, 1864-1871.
- ^{S2}C. Chaudhari, H. Imatome, Y. Nishida, K. Sato and K. Nagaoka, *Catal. Commun.*, 2019, **126**, 55–60.