

## One-pot synthesis of cyclohexylamine and *N*-aryl pyrroles via hydrogenation of nitroarenes over Pd<sub>0.5</sub>Ru<sub>0.5</sub>-PVP catalyst

Chandan Chaudhari,<sup>\*a</sup> Katsutoshi Sato,<sup>a,b</sup> Yasuyuki Ikeda,<sup>c</sup> Kenji Terada,<sup>c</sup> Naoya Abe,<sup>c</sup> and Katsutoshi Nagaoka<sup>\*a</sup>

<sup>a</sup>Department of Chemical Systems Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan

<sup>b</sup>Elements Strategy Initiative for Catalysts and Batteries (ESCIB), Kyoto University, Katsura, Kyoto 615-8520, Japan

<sup>c</sup>Furuya Metal Co., Ltd., Higashitsukuba Niihari Kogyodanchi, 57-4, Sawabe, Tsuchiura City, Ibaraki 300-4104, Japan

\*Corresponding authors

Email address: [nagaoka.katsutoshi@material.nagoya-u.ac.jp](mailto:nagaoka.katsutoshi@material.nagoya-u.ac.jp)

E-mail address: [chaudhari.chandan.subhash@d.mbox.nagoya-u.ac.jp](mailto:chaudhari.chandan.subhash@d.mbox.nagoya-u.ac.jp)

## Experimental Section

### General

All chemicals were purchased from Tokyo Chemical Industry and Wako Pure Chemical Industries (Japan).

### Catalyst preparation

#### i) Wet chemical reduction method<sup>S1</sup>

The monometallic (Pd, Ru) and bimetallic Pd<sub>x</sub>Ru<sub>1-x</sub> catalysts were synthesized as reported previously. Briefly, for the monometallic catalysts, 1 equivalent of metal chloride precursor was dispersed in deionized water (0.0125M, 200mL). Polyvinylpyrrolidone (5 equivalent, K30) was dissolved in 500 mL of ethylene glycol, and the solution was heated to 200 °C. Then the aqueous metal precursor solution was added slowly to the hot ethylene glycol solution of PVP. After the addition was complete, the mixture was stirred continuously for 30 min. The resulting black colloidal solution was cooled to room temperature and then centrifuged to obtain the nanoparticulate catalyst. The Pd<sub>x</sub>Ru<sub>1-x</sub> catalysts were synthesized similarly by controlling the Pd<sup>2+</sup>/Ru<sup>3+</sup> molar ratio.

#### ii) Microwave-assisted wet chemical reduction method<sup>S2</sup>

The metal chloride precursor (1 equivalent) and PVP (5 equivalent) were added to a vessel containing ethylene glycol. The vessel was heated to 180 °C in a microwave (400 W) for 15 min. The metal nanoparticles were separated by centrifuging.

**Table S1. Preparation of mono- and bimetallic catalysts**

Metal (M)	Preparation method	PVP <sup>a</sup> (%)	Metal composition <sup>b</sup> (%)
Pd	Wet chemical reduction	29	-
Ru	Wet chemical reduction	55	-
Pd <sub>0.5</sub> Ru <sub>0.5</sub>	Wet chemical reduction	40	46:56
Pd <sub>0.3</sub> Ru <sub>0.7</sub>	Wet chemical reduction	40	34:66
Pd <sub>0.7</sub> Ru <sub>0.3</sub>	Wet chemical reduction	43	67:33
Rh	Microwave-assisted wet chemical reduction	86	-

<sup>a</sup>Calculated by thermogravimetric analysis.

<sup>b</sup>Determined by ICP-AES.

### Catalyst characterization

The samples were dissolved by the alkaline melting method and then analyzed by ICP-AES. (SPS-3100, Hitachi High-Tech Corporation, Japan).

### Typical procedure for one-pot synthesis of cyclohexylamine

Hydrogenation of nitrobenzene to cyclohexylamine examined in a 10-mL autoclave reactor equipped with a glass tube. In a typical procedure, 1 mmol of nitrobenzene, 1.4 mol% catalyst and 1 mL of cyclohexane were added to the reactor. Then, the reactor purged by H<sub>2</sub> three times before finally pressurized to 2 MPa H<sub>2</sub> and heated to 100 °C with constant stirring at 400 rpm. After completion of the reaction, the reactor cooled down to the room temperature. The obtained products mixture was analyzed by gas chromatograph with flame ionization detector using dodecane an internal standard. The products were confirmed by GC-MS analysis

### Typical procedure for one-pot synthesis of *N*-aryl pyrroles

In a typical procedure, 1 mmol of nitrobenzene, 1 mmol of 2,5-hexanedione, 1.4 mol% catalyst and 1 mL of methanol were introduced to the reactor. The reactor was pressurized to 0.5 MPa and heated to 100 °C.

## References

<sup>S1</sup>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.

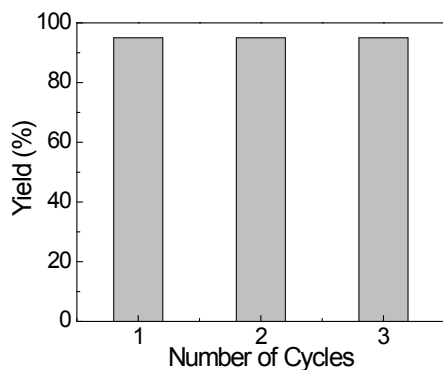
<sup>S2</sup>C. Chaudhari, H. Imatome, Y. Nishida, K. Sato and K. Nagaoka, *Catal. Commun.*, 2019, **126**, 55

**Table S2** Methods for hydrogenation of nitrobenzene to cyclohexylamine

Catalyst	H <sub>2</sub> (MPa)	Additive	Temp. (°C)	Time (h)	Solvent	TON <sup>a</sup>	TOF <sup>b</sup> (h <sup>-1</sup> )	Ref.
Rh/Al <sub>2</sub> O <sub>3</sub>	6.8	--	60	4.5	<i>tert</i> -butanol	11.8	2.6	20
Pd/C	3.5	LiOH	140	6	THF	39.5	6.5	21
Ni/C	2	LiOH	200	4	THF	45.2	11.3	22
Ru@C <sub>60</sub>	3	--	80	7.5	ethanol	143	19.1	23
Ru/NaY	3.5	--	160	0.58	isopropanol	294.1	507	24
<b>Pd<sub>0.5</sub>Ru<sub>0.5</sub>-PVP</b>	<b>2</b>	<b>--</b>	<b>100</b>	<b>6</b>	<b>cyclohexane</b>	<b>65.7</b>	<b>10.9</b>	<b>this work</b>

<sup>a</sup>Turnover number

<sup>b</sup>Turnover frequency



**Figure S1** Recycle study of Pd<sub>0.5</sub>Ru<sub>0.5</sub>-PVP catalyst for the hydrogenation of nitrobenzene to cyclohexylamine under optimized reaction conditions.