

Electronic Supplementary Information (ESI) for

Formal arylation of NH₃ to produce diphenylamines over supported Pd catalysts

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Experimental Section

Instruments and reagents

Gas Chromatography (GC) analyses were performed on Shimadzu GC-2014 equipped with a flame ionization detector (FID) using a capillary column (InertCap5 or TC-Wax) for liquid phase analyses. GC mass spectrometry (GC-MS) spectra were recorded on Shimadzu GCMSQP2010 equipped with a capillary column (InertCap5) at an ionization voltage of 70 eV. Liquid-state ¹H and ¹³C NMR spectra were recorded on JEOL JNM-ECA-500 at 495.1 MHz and 124.5 MHz, respectively, with TMS as an internal standard ($\delta = 0$ ppm). ICP-AES analyses were performed on Shimadzu ICP-8100. TEM observations were performed on JEOL JEM-2000EX. TEM samples were prepared by placing a drop of the suspension on carbon-coated Cu grids. XPS measurements were carried out on JEOL JPS-9000 using Mg K α radiation ($h\nu = 1253.6$ eV, 8 kV, 10 mA). The binding energies were calibrated by using the Au 4f_{7/2} signal at 84.0 eV. BET surface areas were measured by N₂ adsorption at -196 °C using a Micromeritics ASAP 2010 instrument. Al₂O₃ (BET surface area: 160 m² g⁻¹, Cat. No. KHS-24, Sumitomo Chemical), TiO₂ (BET surface area: 316 m² g⁻¹, Cat. No. ST-01, Ishihara Sangyo Kaisya), ZrO₂ (BET surface area: 9 m² g⁻¹, Cat. No. 37022, Nacalai Tesque), CeO₂ (BET surface area: 111 m² g⁻¹) LDH (Mg₆Al₂(OH)₁₆CO₃·4H₂O, BET surface area: 51 m² g⁻¹, Tomita Pharmaceutical Co., Ltd.), Pd/C (Lot. No. 217-024030, NE CHEMCAT), Pt/Al₂O₃ (Lot. No. 137-90020, NE CHEMCAT), and Ru/Al₂O₃ (Lot. No. SH-KO 362-02, NE CHEMCAT) were commercially available. Solvents and substrates were obtained from Kanto Chemical, TCI, Wako, FLUKA, or Aldrich (reagent grade), and purified prior to the use, if necessary (See: *Purification of Laboratory Chemicals*, 3rd ed. (Eds.: D. D. Perrin, W. L. F. Armarego), Pergamon Press, Oxford, 1988.).

Preparation of catalysts

Pd/Al₂O₃ was prepared as follows. Al₂O₃ (2.0 g) was added to a 60 mL aqueous solution of PdCl₂ (8.3 mM) and KCl (two equivalents with respect to PdCl₂, 16.7 mM). The mixture was vigorously stirred at room temperature for 15 min. Then, the pH of the mixture was adjusted to 10.0 by using an aqueous solution of NaOH (1.0 M, *ca.* 1.5 mL), and the resulting slurry was further stirred for 24 h at room temperature. The solid was then filtered off, washed with water (3 L), and dried in vacuo overnight to afford the hydroxide precursor Pd(OH)_x/Al₂O₃. By the reduction of Pd(OH)_x/Al₂O₃ using H₂ (1 atm) at 150 °C for 30 min, Pd/Al₂O₃ was obtained. The XPS spectrum of Pd/Al₂O₃ showed the binding energies of Pd 3d_{3/2} and 3d_{5/2} at 340.4 eV and 335.0 eV, respectively (Fig. S6). This indicated the Pd²⁺ species in the hydroxide precursor were reduced to Pd⁰ by the H₂ treatment. The similar procedure was applied to the preparation of the other supported Pd catalysts. The loading amounts (determined by ICP-AES analyses) and the average particles sizes of Pd (determined by TEM analyses) are summarized in Table S5. Au/Al₂O₃, Cu/Al₂O₃, Rh/Al₂O₃, and Pd–Fe/Al₂O₃ were also prepared by the similar procedure.

Catalytic reactions

A typical procedure for the reaction: Into a Schlenk tube (volume: *ca.* 20 mL) were successively placed Pd/Al₂O₃ (Pd: 1.6 mol% with respect to the cyclohexanone), urea (0.5 mmol), H₂O (10 μL), cyclohexanone (**1a**, 1.0 mmol), diglyme (2 mL), and a Teflon-coated magnetic stir bar (without a stir bar when the reuse experiment was carried out). Then, a balloon partially filled with Ar was connected to the reactor. The reaction was carried out at 150 °C for 24 h with stirring. When the reuse experiment was carried out, the reaction mixture was stirred by the laboratory shaker. After the reaction was completed, an internal standard (biphenyl) was added to the reaction mixture, and the conversion of cyclohexanone and the product yields were determined by GC analysis. As for the isolation of the products, an internal standard was not added. After the reaction, the catalyst was filtered off (>85% recovery). The filtrate was evacuated to remove diglyme while heating at 60 °C. The crude products were subjected to column chromatography on silica gel (see Product data for the eluent utilized), giving the pure diarylamine products. The products were identified by the GC-MS and/or NMR (¹H and ¹³C) analyses. The retrieved catalyst was washed with acetone then with water, and heated at 150 °C for 30 min under H₂ (1 atm) prior to being used for the reuse experiment. The detection of hydrogen in the gas-phase was carried out with MS analysis. The quantification of hydrogen gas formation was performed by measurement of the evolved gas volume.

Product data

Diphenylamine (2a), (CAS No. 122-39-4): A mixture of toluene and *n*-hexane (toluene : *n*-hexane = 75 : 25) was utilized as the eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ = 7.28–7.24 (m, 4H), 7.08–7.05 (m, 4H), 6.94–6.91 (m, 2H), 5.69 (brs, 1H); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS): δ = 143.1, 129.3, 121.0, 117.8; MS (70 eV, EI): *m/z* (%): 170 (18), 169 (100) [*M*⁺], 168 (80), 167 (42), 166 (7), 141 (7), 139 (5), 115 (6), 84 (6), 83 (28), 77 (14), 66 (10), 65 (8), 59 (6), 51 (14), 39 (6).

***o,o'*-Ditolylamine (2b), (CAS No. 617-00-5):** MS (70 eV, EI): *m/z* (%): 198 (15), 197 (100) [*M*⁺], 196 (19), 194 (5), 182 (31), 181 (17), 180 (29), 179 (5), 167 (12), 106 (18), 105 (6), 104 (28), 98 (9), 97 (17), 93 (8), 91 (7), 90 (10), 84 (6), 77 (7), 65 (6).

***m,m'*-Ditolylamine (2c), (CAS No. 626-13-1):** MS (70 eV, EI): *m/z* (%): 198 (16), 197 (100) [*M*⁺], 196 (18), 182 (10), 181 (21), 180 (11), 167 (9), 97 (8), 91 (6), 77 (6), 65 (6).

***p,p'*-Ditolylamine (2d), (CAS No. 620-93-9):** MS (70 eV, EI): *m/z* (%): 198 (17), 197 (100) [*M*⁺], 196 (54), 182 (5), 181 (11), 180 (13), 98 (8), 96 (15), 91 (17), 90 (5).

4,4'-bis-(*tert*-Butylphenyl)amine (2e), (CAS No. 4627-22-9): MS (70 eV, EI): *m/z* (%): 282 (7), 281 (33) [*M*⁺], 267 (22), 266 (100), 250 (9), 236 (6), 126 (10), 112 (6), 98 (24), 57 (6).

2,2',5,5'-bis-(Dimethylphenyl)amine (2g), (CAS No. 117043-82-0): MS (70 eV, EI): *m/z* (%): 226 (19), 225 (100) [*M*⁺], 224 (10), 210 (28), 209 (9), 195 (19), 194 (16), 193 (6), 120 (15), 119 (7), 118 (33), 112 (7), 111 (6), 107 (7), 104 (9), 91 (7), 77 (7).

2,2'-bis-(Methoxyphenyl)amine (2h), (CAS No. 7287-75-4): A mixture of toluene and *n*-hexane (toluene : *n*-hexane = 75 : 25) was utilized as the eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ = 7.38–7.35 (m, 2H), 6.89–6.86 (m, 6H), 7.38–7.35; ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS): δ = 149.0, 132.4, 120.7, 120.1, 115.4, 110.5, 55.6; MS (70 eV, EI): *m/z* (%): 230 (16), 229 (100) [*M*⁺], 214 (10), 184 (13), 183 (88), 182 (35), 170 (10), 154 (8), 115 (8), 107 (5).

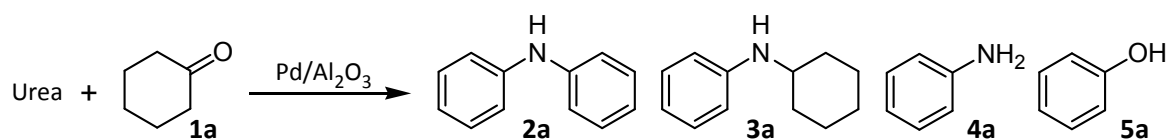
4,4'-bis-(Ethoxyphenyl)amine (2i), (CAS No. 3949-80-2): MS (70 eV, EI): *m/z* (%): 258 (13), 257 (78) [*M*⁺], 229 (18), 228 (100), 201 (7), 200 (36), 154 (6), 143 (6), 142 (5), 127 (7), 117 (6), 115 (6), 65 (6).

4,4'-bis-(Ethoxycarbonylphenyl)amine (2j), (CAS No. 53884-32-5): A mixture of toluene and EtOAc (toluene : EtOAc = 90 : 10) was utilized as the eluent for column chromatography. ¹H NMR

(500 MHz, CDCl₃, 25 °C, TMS): δ = 7.99–7.96 (m, 4H), 7.15–7.12 (m, 4H), 6.68 (brs, 1H), 4.35 (q, J = 7.2 Hz, 4H), 1.38 (t, J = 7.0 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS): δ = 166.4, 145.9, 131.4, 123.2, 116.8, 60.7, 14.4; MS (70 eV, EI): m/z (%): 314 (18), 313 (100) [M^+], 285 (21), 268 (60), 257 (13), 240 (44), 167 (49), 166 (15), 112 (15), 84 (14), 84 (14), 65 (13).

3,3'-bis-(Trifluoromethylphenyl)amine (2i), (CAS No. 7639-70-5): MS (70 eV, EI): m/z (%): 305 (100) [M^+], 306 (16), 235 (13), 284 (13), 216 (8), 286 (7), 304 (7), 167 (7), 236 (5).

4,4'-bis-(tert-Butyldimethylsilyloxyphenyl)amine (2j), (CAS No. 1448526-06-4): A mixture of *n*-hexane and chloroform (*n*-hexane : chloroform = 70 : 30) was utilized as the eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ = 6.87–6.84 (m, 4H), 6.75–6.71 (m, 4H), 5.26 (brs, 1H), 0.98 (s, 18H), 0.18 (s, 12H); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS): δ = 149.7, 138.2, 120.6, 119.2, 25.7, 18.2, -4.5; MS (70 eV, EI): m/z (%): 429 (100) [M^+], 73 (61), 430 (37), 180 (27), 158 (23), 222 (20), 431 (14), 373 (6), 150 (6), 166 (5), 164 (5), 74 (5).

Table S1 Effect of solvents on the formal arylation using urea and cyclohexanone (**1a**)^a

Entry	Solvent	Yield (%)			
		2a	3a	4a	5a
1	Diglyme	87	3	2	5
2	Mesitylene	72	19	1	2
3	DMA	54	23	3	9
4	NMP	49	21	8	1
5	<i>n</i> -Decane	54	33	2	1

^a Reaction conditions: Pd/Al₂O₃ (Pd: 1.6 mol%), urea (0.5 mmol), water (10 μL), **1a** (1 mmol), solvent (2 mL), Ar (1 atm), 150 °C, 24 h. Yields (based on **1a**) were determined by GC using biphenyl as the internal standard.

Table S2 Effect of temperatures on the formal arylation using urea and cyclohexanone (**1a**)^a

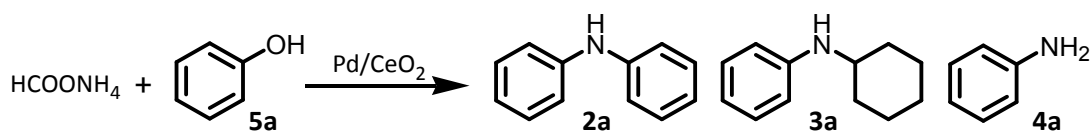
Entry	Temp. (°C)	Yield (%)			
		2a	3a	4a	5a
1	140	10	86	4	<1
2	150	87	3	2	5
3	160	71	2	11	6

^a Reaction conditions: Pd/Al₂O₃ (Pd: 1.6 mol%), urea (0.5 mmol), water (10 μL), **1a** (1 mmol), diglyme (2 mL), Ar (1 atm), 140–160 °C, 24 h. Yields (based on **1a**) were determined by GC using biphenyl as the internal standard.

Table S3 Effect of amounts of urea on the formal arylation using urea and cyclohexanone (**1a**)^a

Entry	Amounts of urea (mmol)	Yield (%)			
		2a	3a	4a	5a
1	0.25	73	2	<1	18
2	0.5	87	3	2	5
3	1.25	40	9	30	1

^a Reaction conditions: Pd/Al₂O₃ (Pd: 1.6 mol%), urea (0.25–1.25 mmol), water (10 μL), **1a** (1 mmol), diglyme (2 mL), Ar (1 atm), 150 °C, 24 h. Yields (based on **1a**) were determined by GC using biphenyl as the internal standard.

Table S4 Optimization of reaction conditions for the formal arylation using phenol (**5a**)^a

Entry	Catalyst (mol%)	Solvent	Temp. (°C)	Yield (%)		
				2a	3a	4^a
1	Pd/CeO ₂ (2)	Mesitylene	140	7	10	8
2	Pd/CeO ₂ (5)	Mesitylene	140	48	5	7
3	Pd/CeO₂ (10)	Mesitylene	140	73	<1	5
4	Pd/CeO ₂ (20)	Mesitylene	140	52	<1	5
5	Pd/Al ₂ O ₃ (10)	Mesitylene	140	48	<1	3
6	Pd/C (10)	Mesitylene	140	42	<1	5
7	Pd/TiO ₂ (10)	Mesitylene	140	40	<1	5
8	Pd/MgO (10)	Mesitylene	140	38	<1	5
9	Pd/ZrO ₂ (10)	Mesitylene	140	21	7	4
10	Pd/CeO ₂ (10)	<i>n</i> -Decane	140	60	16	3
11	Pd/CeO ₂ (10)	Diglyme	140	<1	<1	3
12	Pd/CeO ₂ (10)	DMA	140	<1	<1	2
13	Pd/CeO ₂ (10)	DMF	140	<1	<1	<1
14	Pd/CeO ₂ (10)	Mesitylene	150	31	<1	2
15	Pd/CeO ₂ (10)	Mesitylene	160	4	<1	<1

^a Reaction conditions: Catalyst (Pd: 2–10 mol%), HCOONH₄ (0.6 mmol), **5a** (0.4 mmol), solvent (2 mL), Ar (1 atm), 140–160 °C, 18 h. Yields (based on **5a**) were determined by GC using biphenyl as the internal standard.

Table S5. Pd contents and average particle sizes of various supported Pd nanoparticle catalysts.

Catalyst	Pd content [mmol g ⁻¹]	Average size [nm]
Pd/Al ₂ O ₃	0.236	2.7 ± 0.8
Pd/TiO ₂	0.228	2.3 ± 0.7
Pd/ZrO ₂	0.227	6.4 ± 3.1
Pd/CeO ₂	0.212	2.1 ± 0.9
Pd/LDH	0.237	2.9 ± 0.7
Pd/C	0.223	2.7 ± 0.6
Pd–Fe/Al ₂ O ₃	0.215 (Fe: 0.202)	not measured

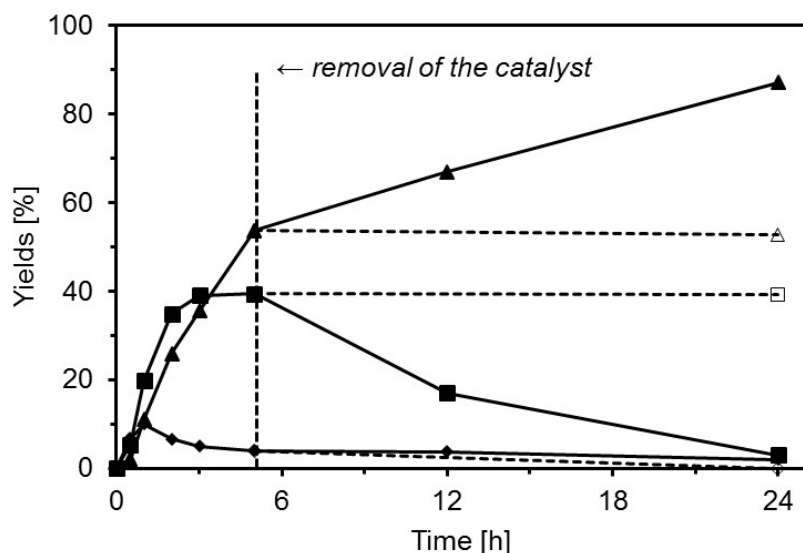


Fig. S1 Effect of removal of the Pd/Al₂O₃ catalyst on the dehydrogenation. The reaction conditions were the same as those described in Table 1. GC yields were determined using *n*-hexadecane as the internal standard. The closed triangles, squares, and diamonds indicate the yields of **2a**, **3a**, and **4a**, respectively, without removal of the catalyst. The open triangles, squares, and diamonds indicate the yields of **2a**, **3a**, and **4a**, respectively, after removal of the catalyst.

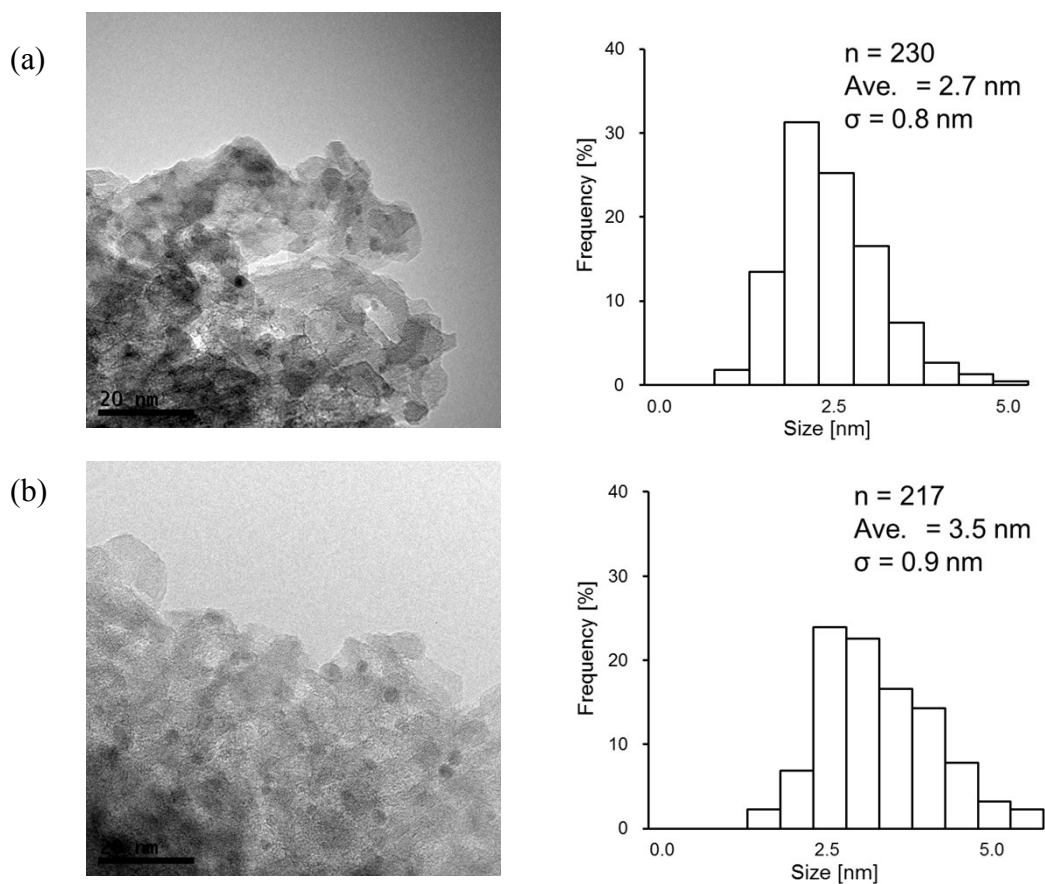


Fig. S2 TEM images and Pd nanoparticle size distributions; (a) the freshly prepared Pd/Al₂O₃ catalyst and (b) the Pd/Al₂O₃ catalyst after the fifth reuse.

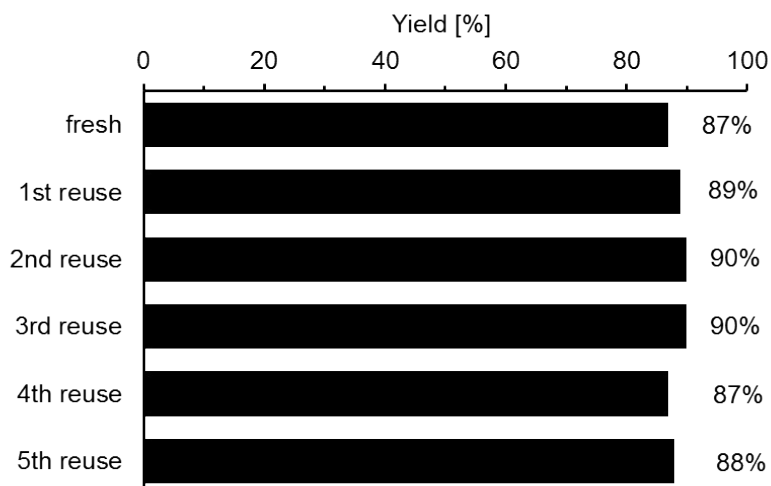


Fig. S3 Pd/Al₂O₃ reuse experiment. The reaction conditions were the same as those described in Table 1. The values indicate the yields of **2a**.

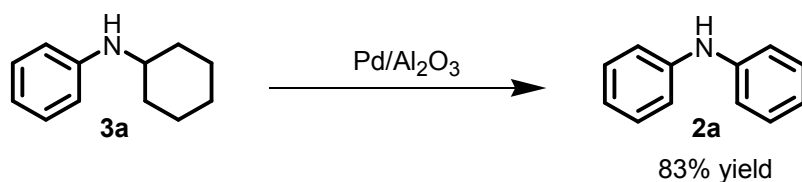


Fig. S4 The reaction of **3a**. Reaction conditions: Pd/Al₂O₃ (3.2 mol% to **3a**), **3a** (0.5 mmol), diglyme (2 mL), Ar (1 atm), 150 °C, 24 h. A Yield was determined by GC using biphenyl as the internal standard.

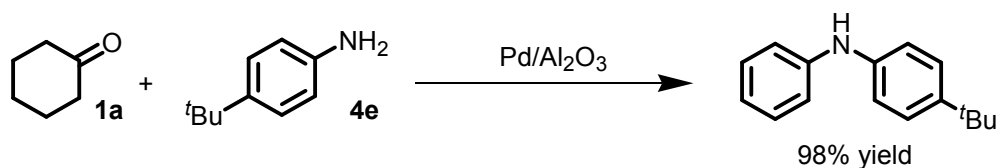


Fig. S5 The reaction of **1a** and **4e**. Reaction conditions: Pd/Al₂O₃ (3.2 mol% to **1a**), **1a** (0.5 mmol), **4e** (0.5 mmol), diglyme (2 mL), Ar (1 atm), 150 °C, 24 h. Yields (based on **1a**) were determined by GC using biphenyl as the internal standard.

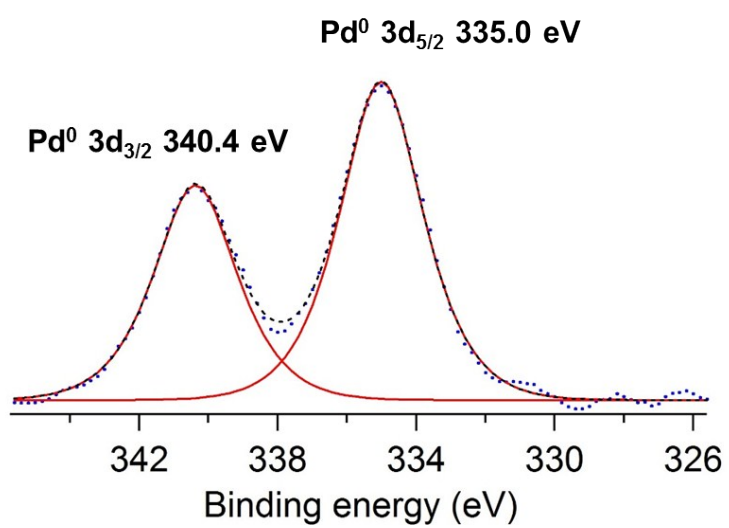


Fig. S6 XPS spectra of the Pd/Al₂O₃ catalyst around 3d components. The blue dots indicates the data points. The red solid and black broken lines indicate the deconvoluted signals, respectively.