Supporting Information

Hydrogenation of Nitriles to Primary Amines Catalyzed by Unsupported Nanoporous Palladium Catalyst: Understanding the Essential Reason for High Activity and Selectivity of Catalyst

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1. General Information

¹H and ¹³C NMR spectra were recorded on either a Varian Inova-400 (400 MHz for ¹H, 100 MHz for ¹³C) or a Bruker Avance II-400 (400 MHz for ¹H, 100 MHz for ¹³C) spectrometer; CDCl₃ was used as a solvent, while tetramethylsilane (TMS) was used as an internal standard. The chemical shifts are reported in ppm downfield (δ) from TMS, and the coupling constants *J* are expressed in Hz. The peak patterns are labeled as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Thin-layer chromatography (TLC) was carried out on SiO₂ (silica gel 60 F254, Merck), and the spots were located with UV light, iodoplatinate reagent, or 1% aqueous KMnO₄. Flash chromatography was carried out on SiO₂ (silica gel 60, 200–300 mesh). GC-MS analysis was performed with gas chromatography-mass spectra (Agilent 7890A/5975C) system (70 eve electron-impact ion source) equipped with an Agilent 19091s-433 (HP-5 ms) capillary column (30 m × 250 µm × 0.25 µm). High resolution mass spectra were recorded on a GC-TOF mass spectrometry.

Arc melting Pd-Al alloy Pd-Al alloy Pd-Al alloy find film with 20-50 Pd-Al alloy find film with 20-50 Pd-Al alloy find film with 20-50 Pd-Al alloy Mt% NaOH solution Nanoporous Pd Pd-Al alloy Nanoporous Pd

2. Preparation of PdNPore Catalyst

Figure S1. Schematic illustration of the fabrication process of nanoporous palladium catalyst.

3. Characterization of Catalyst

The SEM, TEM, HAADF-STEM, and EDX spectra of the fresh catalyst PdNPore and the catalyst PdNPore after six runs are shown in Figure S2 (a–h). These results obtained clearly revealed that the fresh catalyst PdNPore and the catalyst

PdNPore after six runs were essentially same.



Figure S2. SEM images of (a) fresh PdNPore and (b) PdNPore after six runs; TEM images of (c) fresh PdNPore and (d) PdNPore after six runs; HAADF-STEM images of (e) fresh PdNPore and (f) PdNPore after six runs; EDX images of (g) fresh PdNPore and (h) PdNPore after six runs.

The results obtained from the N_2 adsorption-desorption experiment (Figure S3a) revealed that the catalyst PdNPore possesses a high Brunauer-Emmett-Teller (BET) surface area (41 m²/g) due to its porous structure. The pore size distribution of PdNPore was 3.6 nm as determined from the adsorption branch of isotherms based on density functional theory (DFT) method. The results of N_2 adsorption-desorption of PdNPore after six runs are shown in Figures S3b. The results for the fresh one and that after six runs were essentially same.



Figure S3. Nitrogen adsorption/desorption isotherm and corresponding pore size distribution curve (inset) of (a) fresh PdNPore and (b) PdNPore after six runs.

The XPS spectrum of the freshly prepared PdNPore catalyst showed the binding energies of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ at 335.55 and 340.80 eV, respectively (Figure S4a), which higher than those of Pd 3d in metallic palladium.¹ Figure S4b presents the Xray photoelectron spectra of Al 2p in metallic Al and PdNPore. Two kinds of Al 2p signals located at 75.55 and 72.75 eV were observed when metallic Al was subjected to X-ray photoelectron spectroscopy. The former signal was assigned to aluminum oxide, and the latter was assigned to metallic Al.² This result indicated that some Al atoms of metallic Al were oxidized during the determination. The core-level spectrum of Al 2p in PdNPore showed a peak with a binding energy of 74.55 eV, which was assigned to aluminum oxide. The binding energy of Al 2p in PdNPore shifted to a binding energy lower than that of normal aluminum oxide. No peak of Al 2p at approximately 72.75 eV was observed in the X-ray photoelectron spectrum of PdNPore, indicating that the residual A1 in PdNPore transformed into aluminum oxide during dealloying and drying. The upshift of the binding energy for Pd 3d in PdNPore can be ascribed to the transfer of electrons from Pd atoms to aluminum oxides derived from residual Al. The XPS spectra of PdNPore after six runs are shown in Figures S4 (c and d). The results for the fresh one and that after six runs were essentially same.



Figure S4. XPS spectra: (a) Pd 3*d* and (b) Al 2*p* of fresh PdNPore; (c) Pd 3*d* and (d) Al 2*p* of PdNPore after six runs.



Figure S5. Deconvoluted XPS spectra of Pd 3d of fresh PdNPore.

4. Activity Test

The 18% conversion of **1a** was observed with a TOF of 278 h⁻¹ using the PdNPore catalyst when the reaction time was shortened to 5 h. The 14% conversion of **1a** was observed with a TOF of 113 h⁻¹ when the Pd/C catalyst was used instead of the PdNPore catalyst. These results clearly indicated that the activity of the PdNPore catalyst is higher than those of the commercially available catalyst.

Catalyst	Conversion (%)	TOF (h ⁻¹)
PdNPore	18	278
Pd/C	14	113

5. Procedure for Hydrogenation of 4-Formylbenzonitrile to 4-(Hydroxymethyl)benzylamine

PdNPore (1.6 mg, 3 mol %), 4-formylbenzonitrile (**1y**, 65.6 mg, 0.5 mmol), and ethanol (EtOH, 3 mL) were placed in a 25 mL autoclave with a magnetic stir bar under N₂ atmosphere. The autoclave was purged thrice with H₂ gas, filled with H₂ to 5 atm pressure, and reaction mixture was stirred at 50 °C for 24 h. Then, the H₂ gas was replenished to 5 atm again, and the reaction mixture was stirred at 50 °C for another 24 h. The remaining H₂ was vented and the resulting mixture was evaporated in vacuo to obtain the crude product, which was subsequently purified via silica gel chromatography (eluent: ethyl acetate/methanol = 20:1) to afford 4-(hydroxymethyl) benzylamine (**3**y) as a white solid.



6. Deuterium-hydrogen Exchange Reaction

PdNPore (1.6 mg, 3 mol%) and C_2D_5OD (2 mL) were placed in a 25 mL autoclave with a magnetic stir bar under N₂ atmosphere. The autoclave was purged thrice with H₂ gas, filled with H₂ to 5 atm pressure, and stirred at 50 °C for 12 h. Then, the gas mixture generated was detected by GC-MS.



Figure S6. Mass spectrum of deuterium-hydrogen exchange reaction.

7. Characterization Data of Products

Benzylamine (2a)³



Yellow oil (48.8 mg, 91% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.35–7.20 (m, 5H), 3.84 (s, 2H), 1.54 (br, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 143.3, 128.6, 127.1, 126.8, 46.5.

4-Methylbenzylamine (2b)³



Colorless oil (53.9 mg, 89% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 2H), 2.34 (s, 3H), 2.06 (br, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 140.1, 136.6, 129.4, 127.2, 46.2, 21.2.

3-Methylbenzylamine (2c)³



Colorless oil (52.1 mg, 86% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.28–7.22 (m, 1H), 7.16–7.05 (m, 3H), 3.84 (s, 2H), 2.38 (s, 3H), 1.83 (br, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 143.1, 138.0, 128.4, 127.8, 127.5, 124.0, 46.3, 21.3.

4-Methoxybenzylamine (2d)³



Yellow oil (58.3 mg, 85% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.23 (d, J = 6.8 Hz, 2H), 6.87 (d, J = 6.8 Hz, 2H), 3.80 (s, 5H), 1.60 (br, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 158.7, 135.7, 128.4, 114.1, 55.4, 46.0.

3-Methoxybenzylamine (2e)³



Yellow oil (49.4 mg, 72% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.31–7.26 (m, 1H), 6.94–6.88 (m, 2H), 6.84–6.79 (m, 1H), 3.87 (s, 2H), 3.84 (s, 3H), 1.69 (br, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 160.0, 145.1, 129.7, 119.5, 112.7, 112.4, 55.3, 46.6.

2-Methoxybenzylamine (2f)⁴



Yellow oil (41.2 mg, 60% yield). ¹H NMR (CDCl₃, 400 MHz): δ 7.27–7.19 (m, 2H), 6.94–6.85 (m, 2H), 3.86–3.81 (br, 5H), 2.07 (br, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 157.6, 130.1, 128.7, 128.3, 120.7, 110.4, 55.3, 42.7.

4-Fluorobenzylamine (2g)⁵



Yellow oil (51.3 mg, 82% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.35–7.30 (m, 2H), 7.10–6.95 (m, 2H), 3.79 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 162.1 (d, ¹*J*_{*C*-*F*} = 243.3 Hz), 135.7, 129.9 (d, ³*J*_{*C*-*F*} = 8.0 Hz), 115.3 (d, ²*J*_{*C*-*F*} = 21.1 Hz), 52.3.

4-Methoxycarbonylbenzylamine (2h)⁶



Yellow oil (68.6 mg, 83% yield). ¹H NMR (CDCl₃, 400 MHz): δ 8.02 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 3.95 (s, 2H), 3.92 (s, 3H), 1.58 (br, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 167.1, 148.5, 129.9, 128.8, 127.0, 52.1, 46.3.

4-(Aminomethyl)phenyl trifluoromethanesulfonate (2i)



White solid (108.5 mg, 85% yield), mp 147–149 °C. ¹H NMR (CD₃CN, 400 MHz): δ 7.38–7.33 (m, 4H), 6.49 (br, 2H), 4.06 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 131.9,

129.0, 128.9, 128.7, 120.4 (q, J = 254.2 Hz), 117.1. IR (neat): 3156.97, 1732.53, 1618.28, 1401.24, 1245.34, 1165.72, 1031.38, 864.69, 748.96, 698.77, 635.77, 517.80. HRMS (EI) Calcd for C₈H₈F₃NO₃S: 255.0177 [M]⁺; found: 255.0171.

2-Naphthylmethylamine (2j)⁶



Yellow oil (62.1 mg, 79% yield). ¹H NMR (CDCl₃, 400 MHz): δ 7.85 (d, *J* = 8.0 Hz, 3H), 7.78 (s, 1H), 7.52–7.43 (m, 3H), 4.08 (s, 2H), 1.79 (br, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 140.2, 133.6, 132.7, 128.4, 127.8, 127.8, 126.2, 125.9, 125.7, 125.4, 46.5.

4-(Aminomethyl)pyridine (2k)⁷

[∼]NH₂

Colorless oil (43.3 mg, 80% yield). ¹H NMR (CDCl₃, 400 MHz): δ 8.29 (d, J = 6.0 Hz, 2H), 7.02 (d, J = 6.0 Hz, 2H), 3.65 (s, 2H), 1.42 (br, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 151.8, 149.6, 121.8, 45.0.

Furan-2-ylmethanamine (21)⁸

Colorless oil (35.45 mg, 73% yield). ¹H NMR (CDCl₃, 400 MHz): δ 7.21 (d, J = 1.2 Hz, 1H), 6.19–6.15 (m, 1H), 5.99 (d, J = 3.2 Hz, 1H), 3.66 (s, 2H), 1.33 (br, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 156.7, 141.4, 110.1, 104.8, 39.2.

Phenethylamine (2m)⁹



Yellow oil (53.3 mg, 88% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.33–7.26 (m, 2H), 7.25–7.17 (m, 3H), 2.93 (t, *J* = 6.8 Hz, 2H), 2.82 (t, *J* = 6.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 140.0, 128.8, 128.6, 126.2, 51.1, 36.4.

4-Methylphenethylamine (2n)¹⁰



Yellow oil (57.5 mg, 85% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.13–7.05 (m, 4H), 2.89 (t, J = 7.2 Hz, 2H), 2.78 (t, J = 7.2 Hz, 2H), 2.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 136.9, 135.7, 129.2, 128.7, 51.3, 35.9, 21.1.

3-Methylphenethylamine (20)¹¹



Yellow oil (55.4 mg, 82% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.09–7.02 (m, 1H), 6.93–6.84 (m, 3H), 2.78 (t, J = 7.2 Hz, 2H), 2.65 (t, J = 7.2 Hz, 2H), 2.21 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 140.0, 137.9, 129.5, 128.4, 126.9, 125.7, 51.2, 36.4, 21.4.

4-Methoxyphenethylamine (2p)¹²



Yellow oil (62.8 mg, 83% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.06 (d, J = 8.4, 2H), 6.80 (d, J = 8.8 Hz, 2H), 3.77 (s, 3H), 2.84 (t, J = 7.2 Hz, 2H), 2.71 (t, J = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 158.1, 132.1, 129.6, 113.9, 55.3, 51.3, 35.5.

3,4-Dimethoxyphenethylamine (2q)¹³



Yellow oil (70.7 mg, 78% yield). ¹H NMR (400 MHz, CDCl₃): δ 6.79–6.74 (m, 1H), 6.71–6.66 (m, 2H), 3.85 (s, 6H), 2.87 (t, *J* = 7.2 Hz, 2H), 2.73 (t, *J* = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 148.9, 147.4, 132.5, 120.5, 111.9, 111.2, 55.9, 55.8, 51.2, 35.9.

4-Fluorophenethylamine (2r)¹²



Yellow oil (59.8 mg, 86% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.16–7.10 (m, 2H), 7.05–6.90 (m, 2H), 2.88 (t, J = 7.2 Hz, 2H), 2.77 (t, J = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 161.6 (d, ¹ J_{C-F} = 242.4 Hz), 135.7 (d, ⁴ J_{C-F} = 3.2 Hz), 130.1 (d, ³ J_{C-F} = 7.8 Hz), 115.3 (d, ² J_{C-F} = 21.0 Hz), 51.2, 35.6.

4-Trifluoromethylphenethylamine (2s)¹²



Yellow oil (83.2 mg, 88% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.52 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 2.91 (t, J = 6.0 Hz, 2H), 2.83 (t, J = 6.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 144.2, 129.3, 129.1 (q, ² J_{C-F} = 32.2 Hz), 125.5 (q, ³ J_{C-F} = 3.7 Hz), 123.1, 50.7, 36.3.

1-Hexaneamine (2u)9



Colourless oil (44.0 mg, 87% yield). ¹H NMR (400 MHz, CDCl₃): δ 2.59 (t, J = 7.2 Hz, 2H), 1.51–1.43 (m, 2H), 1.35–1.27 (m, 6H), 0.87 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 50.2, 31.9, 30.1, 27.2, 22.8, 14.2.

Cyclohexanemethanamine (2v)⁹



Yellow oil (47.5 mg, 84% yield). ¹H NMR (400 MHz, CDCl₃): δ 2.41 (d, J = 6.8 Hz, 2H), 1.75–1.63 (m, 5H), 1.52–1.40 (m, 1H), 1.30–1.08 (m, 3H), 0.95–0.82 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 57.0, 37.9, 31.6, 26.8, 26.2.

4-(Hydroxymethyl)-benzonitrile (2y)¹⁴



White solid (61.2 mg, 92% yield), mp 41–43 °C, (lit. mp 41–42 °C). ¹H NMR (400 MHz, CDCl₃): δ 7.61 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 4.75 (s, 2H), 2.78 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 146.5, 132.3, 127.0, 118.9, 110.8, 64.0.

4-(Hydroxymethyl)-benzylamine (3y)¹⁵



White solid (54.9 mg, 80% yield), mp 80–82 °C, (lit. mp 79 °C). ¹H NMR (400 MHz, CDCl₃): δ 7.36–7.25 (m, 4H), 4.68 (s, 2H), 3.86 (s, 2H), 1.67 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 142.7, 139.5, 127.3, 127.3, 65.1, 46.2.

4-Aminobenzonitrile (2z)¹⁶



Yellow solid (54.3 mg, 92% yield), mp 82–84 °C, (lit. mp 83–86 °C). ¹H NMR (400 MHz, CDCl₃): δ 7.42–7.38 (m, 2H), 6.66–6.62 (m, 2H), 4.21 (br, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 150.5, 133.8, 120.2, 114.5, 100.1.

8. References

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9. Copies of ¹H and ¹³C NMR Spectra of Products











¹³C NMR, 100 MHz, CDCl₃





















¹³C NMR, 100 MHz, CDCl₃





S21



S22











S27





S29















¹³C NMR, 100 MHz, CDCl₃









¹³C NMR, 100 MHz, CDCl₃

