Supporting Information

Reductive amination of Aldehydes and Amines with an Efficient Catalyst Pd/NiO

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I. Experimental Section:

All the solvents and chemicals were obtained commercially and were used as received. NMR spectra were measured using a Bruker 400 MHz (^1H) instruments, and the spectra data were recorded in CDCl_3 and the chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) as internal standard. MS was in general measured on a HP 6890/5973 GC-MS. Powder X-ray diffraction (XRD) patterns were recorded with a Siemens D/max-RB powder X-ray diffractometer, which uses $\text{Cu-K}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). Scans were made in the 2θ range of $10\text{--}90^\circ$ with a step of 2° . The elemental analysis of the sample was carried out by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) with a 3510 ICP-AES instrument of ARL Co. USA. According to the analysis, the loadings of fresh samples were as follows: 1.1 wt% Pd/NiO. X-ray photoelectron spectra (XPS) were collected using VG ESCALAB 210 instrument with contaminated C as internal standard ($\text{C}_{1s}=284.8 \text{ eV}$).

Preparation of the NiO nanoparticles

The catalyst samples were prepared starting from sol-gel polymerization of resorcinol and formaldehyde with Na_2CO_3 as a catalyst with 50%Ni-doped monolithic carbon aerogels. Typically, resorcinol (2.20 g, 20 mmol), formaldehyde (3.25 g, 40 mmol, 36.5% in water, methanol stabilized) and 6 mL distilled water were added into a 100 mL PTFE autoclave and the mixture was stirred for 0.5 h. Subsequently, an aqueous solution of 5.8 g $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ was added dropwise and a 0.9M solution of Na_2CO_3 (4 mL) were added into the mixture. After vigorous stirring for 1 h, the autoclave was sealed and kept at 80°C for 1 day. Then the autoclave was cooled to room temperature. The wet gels were placed into a round-bottomed flask and vacuum dried at 130°C for 3 h. After being pyrolyzed at 800°C for 5 h in nitrogen flow (20 mL/min), about 7 g black solid was obtained. Then the black solid was treated at 500°C for 5 h in a flow of oxygen (20 mL/min) to afford the NiO nanoparticles (about 4.1 g).

Preparation of Pd/NiO catalysts

Pd that was supported on NiO was prepared according to a solimmobilization method. For the 1.1 wt% Pd/NiO catalyst, the detailed preparation procedure employed is described below. 0.067 mL an aqueous solution of H_2PdCl_4 (0.067 mL , 35 mg mL^{-1}) was added to distilled water (5 mL). Then, an aqueous solution of PVA (1.2 mL , 5 mg mL^{-1}) was added. After 30 min, a freshly prepared 0.1 M solution of NaBH_4 (NaBH_4/Pd , 4:1 mol/mol) was then added to form a dark-brown sol. After 30 min of sol generation, the colloid was immobilized by adding NiO powder (100 mg). The solution was acidified to pH 1 by sulfuric acid under string conditions and was stirred for another 2 h finally. The resulting solid was washed with distilled water ($3\times 40 \text{ mL}$) and was dried in air at 80°C for 2 h to afford the Pd/NiO catalyst.

Reductive reaction of aldehydes and amines

1.0 mmol amine, 1.0 mmol aldehyde, 2 mL solvent and 20 mg catalyst were added in a 40 mL reaction tube. The above mixture were reacted at 25 °C and at 1 atm H₂ for 12 h. After the reaction, the reaction mixture was detected by GC-MS. The aimed product was obtained by TLC and analysis by NMR.

II. Substrates synthesis:

Synthesis of N-(2-methoxybenzyl)aniline¹

Aniline (93 mg, 1 mmol), 2-methoxybenzaldehyde (136 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-(2-methoxybenzyl)aniline was obtained (207 mg, Isolated yield = **97%**). ¹H NMR (400MHz, CDCl₃, ppm): **δ 7.31-7.14 (m, 4H), δ 6.92-6.87 (m, 2H), δ 6.72-6.65 (m, 3H), δ 4.33 (s, 2H), δ 4.30 (br s, 1H), δ 3.86 (s, 3H);**

Synthesis of N-(3-methoxybenzyl)aniline²

Aniline (93 mg, 1 mmol), 3-methoxybenzaldehyde (136 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-(3-methoxybenzyl)aniline was obtained (198 mg, Isolated yield = **93%**). ¹H NMR (400MHz, CDCl₃, ppm): **δ 7.28-7.15 (m, 4H), δ 6.97-6.83 (m, 2H), δ 6.82-6.63 (m, 3H), δ 4.30 (s, 2H), δ 4.10 (br s, 1H), δ 3.79 (s, 3H);**

Synthesis of N-(4-methoxybenzyl)aniline¹

Aniline (93 mg, 1 mmol), 4-methoxybenzaldehyde (136 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-(4-methoxybenzyl)aniline was obtained (198 mg, Isolated yield = 93%). ¹H NMR (400MHz, CDCl₃, ppm): δ 7.30-7.16 (m, 4H), δ 6.89-6.87 (m, 2H), δ 6.73-6.63 (m, 3H), δ 4.25 (s, 2H), δ 3.95 (br s, 1H), δ 3.80 (s, 3H);

Synthesis of N-(2-methylbenzyl)aniline¹

Aniline (93 mg, 1 mmol), 2-methylbenzaldehyde (120 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-(2-methylbenzyl)aniline was obtained (193 mg, Isolated yield = 98%). ¹H NMR (400MHz, CDCl₃, ppm): δ 7.34-7.23 (m, 3H), δ 7.21-7.15 (m, 3H), δ 6.74-6.62 (m, 3H), δ 4.26 (s, 2H), δ 3.90 (br s, 1H), δ 2.37 (s, 3H);

Synthesis of N-(3-methylbenzyl)aniline³

Aniline (93 mg, 1 mmol), 3-methylbenzaldehyde (120 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-(3-methylbenzyl) aniline was obtained (189 mg, Isolated yield = 96%). ¹H NMR (400MHz, CDCl₃, ppm): δ 7.25-7.08 (m, 6H), δ 6.74-6.63 (m, 3H), δ 4.28(s, 2H), δ 4.06 (br s, 1H), δ 2.35 (s, 3H);

Synthesis of N-(4-methylbenzyl)aniline¹

Aniline (93 mg, 1 mmol), 4-methylbenzaldehyde (120 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-(4-methylbenzyl)aniline was obtained (189 mg, Isolated yield = 96%). ¹H NMR (400MHz, CDCl₃,

ppm): δ 7.27-7.14 (m, 6H), δ 6.73-6.62 (m, 3H), δ 4.28 (s, 2H), δ 3.98 (br s, 1H), δ 2.34 (s, 3H);

Synthesis of N-(4-fluorobenzyl)aniline¹

Aniline (93 mg, 1 mmol), 4-fluorobenzaldehyde (124 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-(4-fluorobenzyl)aniline was obtained (195 mg, Isolated yield = 97%). ¹H NMR (400MHz, CDCl₃, ppm): δ 7.35-7.31 (m, 2H), δ 7.24-7.0 (m, 4H), δ 6.74-6.61 (m, 3H), δ 4.29(s, 2H), δ 4.03 (br s, 1H);

Synthesis of N-(4-chlorobenzyl)aniline¹

Aniline (93 mg, 1 mmol), 4-chlorobenzaldehyde (140 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-(4-chlorobenzyl)aniline was obtained (188 mg, Isolated yield = 87%). ¹H NMR (400MHz, CDCl₃, ppm): δ 7.30-7.15 (m, 6H), δ 6.74-6.60 (m, 3H), δ 4.31 (s, 2H), δ 4.09 (br s, 1H);

Synthesis of N-(3-chlorobenzyl)aniline⁴

Aniline (93 mg, 1 mmol), 3-chlorobenzaldehyde (140 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-(3-chlorobenzyl)aniline was obtained (204 mg, Isolated yield = 94%). ¹H NMR (400MHz, CDCl₃, ppm): δ 7.37-7.16 (m, 6H), δ 6.76-6.61 (m, 3H), δ 4.32(s, 3H);

Synthesis of N-(furan-2-ylmethyl)aniline¹

Aniline (93 mg, 1 mmol), furan-2-carbaldehyde (96 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-(furan-2-ylmethyl)aniline was obtained (164 mg, Isolated yield = 95%). ¹H NMR (400MHz, CDCl₃, ppm): δ 7.36 (d, J=0.92Hz, 1H), δ 7.21-7.17 (t, J=7.6Hz, 2H), δ 6.76-6.72 (t, J=7.26Hz, 1H), δ 6.68-6.67 (d, J=7.6Hz, 2H), δ 6.23-6.24 (m, 2H), δ 4.31(s, 2H), δ 4.03 (br s, 1H);

Synthesis of N-butylaniline⁵

Aniline (93 mg, 1 mmol), butyraldehyde (72 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-butylaniline was obtained (146 mg, Isolated yield = 98%). ¹H NMR (400MHz, CDCl₃, ppm): δ 7.25-7.16 (m, 2H), δ 6.69 (t, J=7.2Hz, 1H), δ 6.62-6.60 (d, J=8.4Hz, 2H), δ 3.65 (br s, 1H), δ 3.01-3.12 (t, J=7.2Hz, 2H), δ 1.64-1.55 (m, 2H), δ 1.54-1.38 (m, 2H), δ 0.97 (t, J=7.2Hz, 3H);

Synthesis of N-benzyl-naphthalen-1-amine⁶

benzaldehyde (106 mg, 1 mmol), naphthalen-1-amine (143 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-benzyl-naphthalen-1-amine was obtained (196 mg, Isolated yield = 84%). ¹H NMR (400MHz, CDCl₃, ppm): δ 7.83-7.79 (m, 2H), δ 7.47-7.24 (m, 9H), δ 6.65-6.62 (d, J=8.0Hz, 1H), δ 4.49(s, 2H), δ 4.01 (br s, 1H);

Synthesis of dibenzylamine⁶

benzaldehyde (106 mg, 1 mmol), phenylmethanamine (107 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, dibenzylamine was obtained (191 mg, Isolated yield = 97%). ¹H NMR (400MHz, CDCl₃, ppm): δ 7.35-7.25 (m, 10H), δ 3.81(s, 4H), δ 1.85 (br s, 1H);

Synthesis of N-benzyl-1-p-tolylmethanamine⁷

benzaldehyde (106 mg, 1 mmol), p-tolylmethanamine (121 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-benzyl-1-p-tolylmethanamine was obtained (194 mg, Isolated yield = 92%). ¹H NMR (400MHz, CDCl₃, ppm): δ 7.40-7.13 (m, 9H), δ 3.81 (s, 2H), δ 3.78(s, 2H), δ 3.32(br s, 1H), δ 2.33 (s, 3H);

Synthesis of N-benzyl-1-phenylethanamine⁴

benzaldehyde (106 mg, 1 mmol), 1-phenylethanamine (121 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-benzyl-1-phenylethanamine was obtained (207 mg, Isolated yield = 98%). ¹H NMR (400MHz, CDCl₃, ppm): δ 7.36-7.22 (m, 10H), δ 3.84-3.79(q, J=6.8 Hz 1H), δ 3.68-3.57 (dd, J=13.2Hz, 6.8 Hz, 2H), δ 1.82(br s, 1H), δ 1.37 (d, J=6.8 Hz, 3H);

Synthesis of N-benzyl-1-(4-methoxyphenyl)methanamine⁶

benzaldehyde (106 mg, 1 mmol), (4-methoxyphenyl)methanamine (137 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-benzyl-1-(4-methoxyphenyl)methanamine was obtained (204mg, Isolated yield = 90%). ¹H NMR (400MHz, CDCl₃, ppm): δ 7.35-7.23 (m, 7H), δ 6.87-6.85 (d, J=8Hz, 2H), δ

3.79-3.78 (7H), δ 2.90 (br s, 1H);

Synthesis of N-benzylpyridin-2-amine⁸

benzaldehyde (106 mg, 1 mmol), pyridin-2-amine (94 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-benzylpyridin-2-amine was obtained (155mg, Isolated yield = 84%). ¹H NMR (400MHz, CDCl₃, ppm): δ 8.11 (s, 1H), δ 7.42-7.26 (m, 6H), δ 6.61-6.58 (t, J=6.4 Hz, 1H), δ 6.39-6.37 (d, J=8.4Hz, 1H), δ 4.97 (br s, 1H), δ 4.51-4.50 (d, J=5.6Hz, 2H);

Synthesis of N-benzyl-1-(furan-2-yl)methanamine⁹

benzaldehyde (106 mg, 1 mmol), furan-2-ylmethanamine (97 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-benzyl-1-(furan-2-yl)methanamine was obtained (172mg, Isolated yield = 92%). ¹H NMR (400MHz, CDCl₃, ppm): δ 7.52-7.24 (m, 6H), δ 6.33-6.32 (dd, J=4Hz, 2.4Hz, 1H), δ 6.21-6.20 (d, J=2.4Hz, 1H), δ 3.81-3.62 (s, 4H), δ 2.94 (br s, 1H);

Synthesis of N-benzyl-2-(piperazin-1-yl)ethanamine¹⁰

benzaldehyde (106 mg, 1 mmol), 2-(piperazin-1-yl)ethanamine (129 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-benzyl-2-(piperazin-1-yl)ethanamine was obtained (215mg, Isolated yield = 98%). ¹H NMR (400MHz, CDCl₃, ppm): δ 7.43-7.25 (m, 5H), δ 3.81 (s, 2H), δ 2.88 (t, J=4.8Hz, 4H), δ 2.70 (t, J=6Hz, 2H), δ 2.50-2.39 (m, 8H);

Synthesis of N-benzylcyclohexanamine¹¹

benzaldehyde (106 mg, 1 mmol), cyclohexanamine (99 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-benzylcyclohexanamine was obtained (185mg, Isolated yield = 98%). ¹H NMR (400MHz, CDCl₃, ppm), δ 7.23-7.45(m, 5H), δ 3.84 (s, 2H), δ 2.97 (s, 1H), δ 2.52 (t, J=10Hz, 1H), δ 1.96-1.12 (m, 10H);

Synthesis of N-benzylheptan-1-amine¹²

benzaldehyde (106 mg, 1 mmol), heptan-1-amine (115 mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-benzylheptan-1-amine was obtained (201mg, Isolated yield = 98%). ¹H NMR (400MHz, CDCl₃, ppm), δ 7.39-7.25 (m, 5H), δ 3.81 (s, 2H), δ 2.80 (br s, 1H), δ 2.65-2.62 (t, J=7.6Hz, 2H), δ 1.26-1.54 (m, 10H), δ 0.884-0.851 (t, J=6.0Hz, 3H);

Synthesis of N-benzyl-dodecan-1-amine¹³

benzaldehyde (106 mg, 1 mmol), dodecan-1-amine (185mg, 1 mmol) and 20 mg 1.1 wt% Pd/NiO were added into a 50 mL reaction tube and reacted at 25 °C under hydrogen atmosphere for 10 h. The crude mixture was purified by filtration and after direct rotary evaporation. Following the procedure above, N-benzyl-dodecan-1-amine was obtained (264mg, Isolated yield = 96%). ¹H NMR (400MHz, CDCl₃, ppm), δ 7.44-7.24 (m, 5H), δ 3.81(s, 2H), δ 2.90 (br s, 1H), δ 2.64 (t, J=7.2Hz, 2H), δ 1.54-1.18 (m, 20H), δ 0.88(t, J=6.4Hz,3H);

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