Electronic Supplementary Material (ESI) for Dalton Transactions

Rapid microwave-assisted sol-gel preparation of Pd-substituted LnFeO$_3$ (Ln = Y, La): Phase formation and catalytic activity

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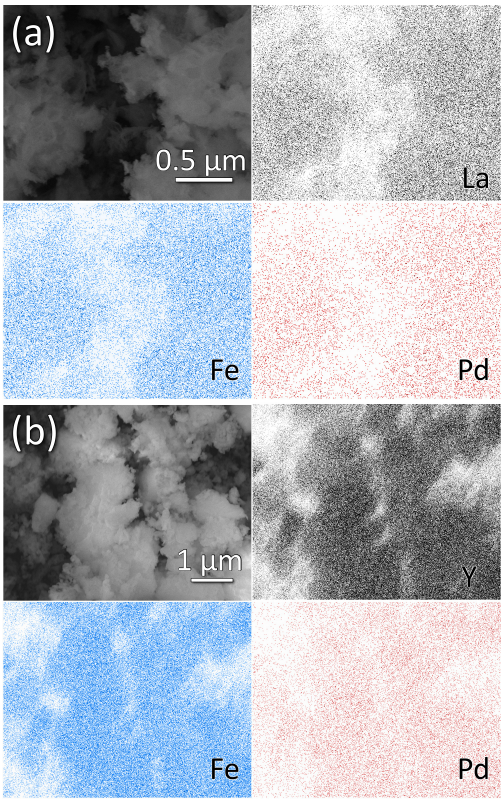
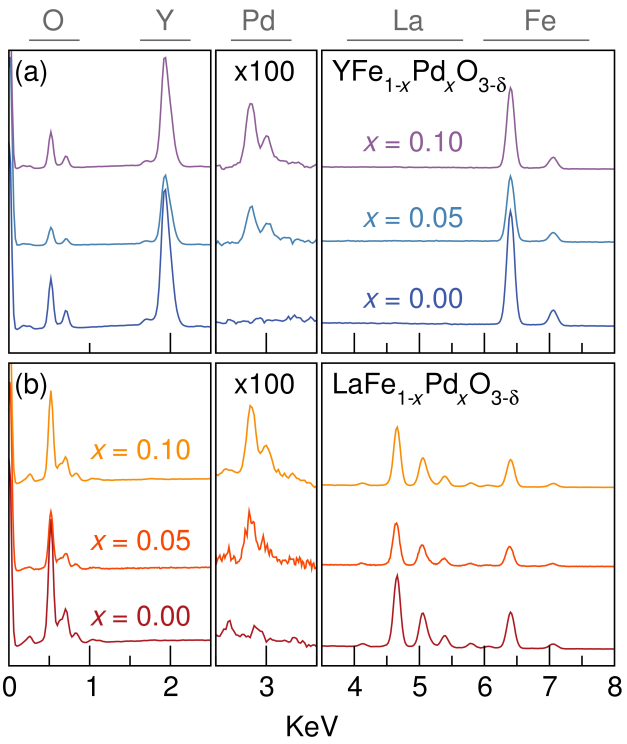
Supplementary information



Energy-dispersive X-ray spectroscopy mapping data of (a) LaFe$_{0.95}$Pd$_{0.05}$O$_{3-\delta}$ and (b) YFe$_{0.95}$Pd$_{0.05}$O$_{3-\delta}$. Uniform distribution of Pd is observed in both samples.



Energy-dispersive X-ray spectroscopy elemental analysis data of (a) $YFe_{1-x}Pd_sO_{3-\delta}$ and (b) $LaFe_{1-x}Pd_sO_{3-\delta}$. The Pd region is magnified 100× to show that Pd content increases with doping concentration.

3-Phenylpyridine (Figure 8(a)). Following the general procedure, a mixture of 3-chloropyridine (95 μL, 1.0 mmol), phenylboronic acid (171 mg, 1.4 mmol), $LaFe_{0.95}Pd_{0.05}O_{3-\delta}$ (2 mg, 0.04 mol%), SPhos (4.1 mg, 1 mol%), K_2CO_3 (193 mg, 1.4 mmol), and the solvent (1:1 i-PrOH/H_2O, 2 mL) was heated to 80°C for 20 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap column; 0-25% EtOAc/hexanes) to provide the title compound as a clear oil (143 mg, 92%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.82 (s, 1H), 8.56 (d, J = 3.5 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 7.4 Hz, 2H), 7.43 (t, J = 7.7 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.30 (dd, J = 4.7 Hz, J = 7.8 Hz, 1H) ppm. ^{13}C NMR (600 MHz, $CDCl_3$) δ: 148.4, 148.3, 137.8, 136.6, 134.3, 129.1, 128.1, 127.1, 123.5 ppm. IR (neat, cm^{-1}): 3030, 1581, 1472, 1450, 1407, 1024, 1005, 812, 712, 698. HRMS-EIMS (m/z): M^+ calcd for $C_{11}H_9N$, 155.0735; found, 155.0733.

3-Phenylpyridine (Figure 8(b)). Following the general procedure, a mixture of 3-bromopyridine (96 μL, 1.0 mmol), phenylboronic acid (171 mg, 1.4 mmol), $LaFe_{0.95}Pd_{0.05}O_{3-\delta}$ (2 mg, 0.04 mol%), SPhos (4.1 mg, 1 mol%), K_2CO_3 (193 mg, 1.4 mmol), and the solvent (1:1 i-PrOH/H_2O, 2 mL) was heated to 80°C for 20 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap column; 0-25% EtOAc/hexanes) to provide the title compound as a clear oil (137 mg, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.74 (s, 1H), 8.47 (d, J = 3 Hz, 1H), 7.74 (d, J = 7.2 Hz, 1H), 7.45 (d, J = 7.2, 2H), 7.34 (t, J = 7.2, 2H), 7.28 (t, J = 7.2 Hz, 1H), 7.22 (dd, J = 4.8 Hz, J = 7.8 Hz, 1H) ppm. ^{13}C NMR (600 MHz, $CDCl_3$) δ: 148.2, 148.1, 137.7, 136.7, 134.5, 129.1, 128.1, 127.1, 123.6 ppm. IR (neat, cm^{-1}): 3031, 1581, 1472, 1450, 1407, 1024, 1005, 812, 710, 696. HRMS-EIMS (m/z): M^+ calcd for $C_{11}H_9N$, 155.0735; found, 155.0731.

3-(3-Methoxyphenyl)pyridine (Figure 8(c)). Following the general procedure, a mixture of 3-chloropyridine (95 μL, 1.0 mmol), 3-methoxyphenylboronic acid (213 mg, 1.4 mmol), $LaFe_{0.95}Pd_{0.05}O_{3-\delta}$ (2 mg, 0.04 mol%), SPhos (4.1 mg, 1 mol%), K_2CO_3 (193 mg, 1.4 mmol), and the solvent (1:1 i-PrOH/H2O, 2 mL) was heated to 80°C for 20 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap column; 0-20% EtOAc/hexanes) to provide the title compound as a clear oil (135 mg, 73%). 1H NMR (600 MHz, $CDCl_3$) δ: 8.81 (s, 1H), 8.54 (d, J = 3.5 Hz, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.33 (t, J = 7.9, 1H), 7.29 (dd, J = 4.9 Hz, J = 7.9, 1H), 7.11 (d, J = 7.7 Hz, 1H), 7.06 (s, 1H), 6.90 (d, J = 8.2 Hz, 1H), 3.80 (s, 3H) ppm. ^{13}C NMR (600 MHz, $CDCl_3$) δ: 160.1, 148.4, 148.1, 139.1, 136.5, 134.5, 130.1, 123.6, 119.5, 113.4, 112.9, 55.3 ppm. IR (neat, cm^{-1}): 1601, 1585, 1470, 1402, 1299, 1047, 1015, 779, 711, 696. HRMS-EIMS (m/z): M^+ calcd for $C_{12}H_{11}NO$, 185.0841; found, 185.0844.

2-(Thiophen-2-yl)pyridine (Figure 8(d)). Following the general procedure, a mixture of 2-bromopyridine (96 μL, 1.0 mmol), 2-thienylboronic acid (179 mg, 1.4 mmol), $LaFe_{0.95}Pd_{0.05}O_{3-\delta}$ (2 mg, 0.04 mol%), SPhos (4.1 mg, 1 mol%), K_2CO_3 (193 mg, 1.4 mmol), and the solvent (1:1 i-PrOH/H2O, 2 mL) was heated to 80°C for 20 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap column; 0-25% EtOAc/hexanes) to provide the title compound as a clear oil (125 mg, 78%). 1H NMR (600 MHz, $CDCl_3$) δ: 8.53 (d, J = 4.8 Hz, 1H), 7.61 (m, 2H), 7.54 (d, J = 3.6 Hz, 1H), 7.35 (d, J = 4.8 Hz, 1H), 7.08 (m, 2H) ppm. ^{13}C NMR (600 MHz, $CDCl_3$) δ: 152.5, 149.5, 144.8, 136.7, 128.0, 127.5, 124.6, 121.9, 118.8 ppm. IR (neat, cm^{-1}): 2920, 2851, 1580, 1560, 1464, 1435, 1421, 992, 853, 712. HRMS-EIMS (m/z): M^+ calcd for C_9H_7NS, 161.0299; found, 161.0306.

2-Methylbiphenyl (Figure 8(e)). Following the general procedure, a mixture of 2-chlorotoluene (117 μL, 1.0 mmol), phenylboronic acid (171 mg, 1.4 mmol), $LaFe_{0.95}Pd_{0.05}O_{3-\delta}$ (2 mg, 0.04

mol%), SPhos (4.1 mg, 1 mol%), K_2CO_3 (193 mg, 1.4 mmol), and the solvent (1:1 i-PrOH/H2O, 2 mL) was heated to 80°C for 20 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap column; 0-2% EtOAc/hexanes) to provide the title compound as a clear oil (112 mg, 67%). 1H NMR (600 MHz, $CDCl_3$) δ: 7.29 (m, 2H), 7.22 (m, 3H), 7.14 (m, 4H), 2.17 (s, 3H) ppm. ^{13}C NMR (600 MHz, $CDCl_3$) δ: 142.1, 142.0, 130.4, 129.9, 129.3, 128.1, 127.3, 126.8, 125.8, 20.5 ppm. IR (neat, cm^{-1}): 3020, 1598, 1478, 1438, 1380, 1072, 1009, 773, 726, 701. HRMS-EIMS (m/z): $[M-H]^+$ calcd for $C_{13}H_{11}$, 167.0861; found, 167.0869

Methyl biphenyl-3-carboxylate (Figure 8(f)). Following the general procedure, a mixture of methyl 3-chlorobenzoate (139 δL, 1.0 mmol), phenylboronic acid (171 mg, 1.4 mmol), $LaFe_{0.95}Pd_{0.05}O_{3-\delta}$ (2 mg, 0.04 mol%), SPhos (4.1 mg, 1 mol%), K_2CO_3 (193 mg, 1.4 mmol), and the solvent (1:1 i-PrOH/H2O, 2 mL) was heated to 80°C for 20 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap column; 0-10% EtOAc/hexanes) to provide the title compound as a clear oil (138 mg, 65%). 1H NMR (600 MHz, $CDCl_3$) δ: 8.17 (s, 1H), 7.89 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 7.3 Hz, 2H), 7.36 (t, J = 7.7 Hz, 1H), 7.32 (t, J = 7.7 Hz, 2H), 7.24 (t, J = 7.4 Hz, 1H), 3.80 (s, 3H) ppm. ^{13}C NMR (600 MHz, $CDCl_3$) δ: 167.0, 141.5, 140.1, 131.5, 130.7, 128.9, 128.8, 128.4, 128.3, 127.8, 127.1, 52.2 ppm. IR (neat, cm^{-1}): 1719, 1454, 1435, 1300, 1110, 1085, 1049, 741, 696, 671. HRMS-EIMS (m/z): M^+ calcd for $C_{14}H_{12}O_2$, 212.0837; found, 212.0846.

3-Methoxybiphenyl (Figure 8(g)). Following the general procedure, a mixture of chlorobenzene (101 μL, 1.0 mmol), 3-methoxyphenylboronic acid (213 mg, 1.4 mmol), $LaFe_{0.95}Pd_{0.05}O_{3-\delta}$ (2 mg, 0.09 mol%), SPhos (4.1 mg, 1 mol%), K_2CO_3 (193 mg, 1.4 mmol), and the solvent (1:1 iPrOH/H2O, 2 mL) was heated to 80°C for 20 h. The crude product was purified via the Biotage SP4 (silica-packed 25 g snap column; 0-12 EtOAc/hexanes) to provide the title compound as a clear oil (94 mg, 51). 1H NMR (600 MHz, $CDCl_3$) δ: 7.62 (d, J = 7.3 Hz, 2H), 7.46 (t, J = 7.7 Hz, 1H), 7.38 (m, 2H), 7.22 (d, J = 7.6 Hz, 1H), 7.17 (s, 1H), 6.93 (dd, J = 2.0 Hz, J = 8.3 Hz, 1H), 3.88 (s, 3H) ppm. ^{13}C NMR (600 MHz, $CDCl_3$) δ: 159.9, 142.8, 141.1, 129.8, 128.8, 127.4, 127.2, 119.7, 112.9, 112.7, 55.3. IR (neat, cm^{-1}): 1598, 1573, 1477, 1420, 1295, 1212, 1053, 1038, 1019, 697. HRMS-EIMS (m/z): M^+ calcd for $C_{13}H_{12}O$, 184.0888; found, 184.0893.