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Highly Active Thiol-Functionalized SBA-15 Supported Palladium Catalyst for Sonogashira and Suzuki-Miyaura Cross-Coupling Reactions

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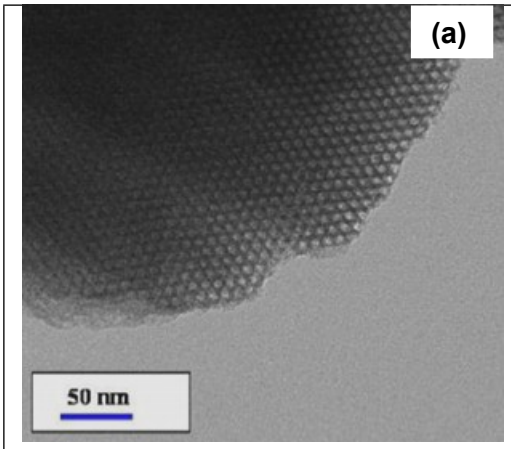

Fig. 1. TEM image of parent SBA-15 silica.

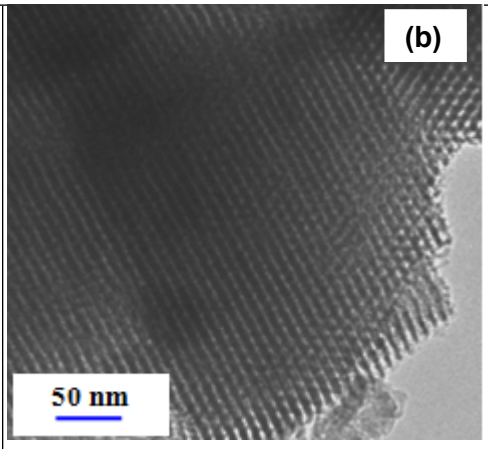

Fig. 2. TEM image of SBA-15-supported Pd-catalyst **2**.

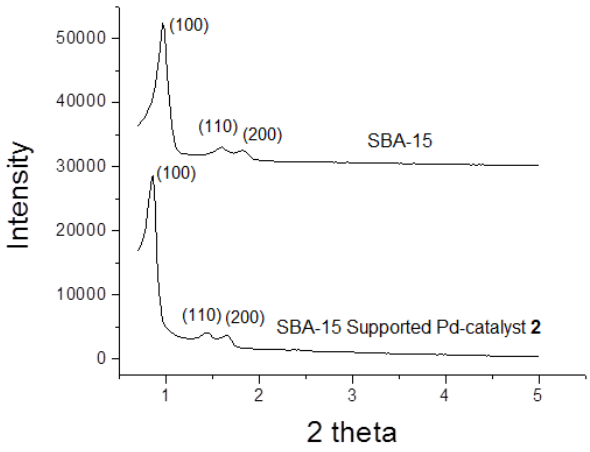

Fig. 3. XRD pattern of SBA-15-supported Pd-catalyst **2**

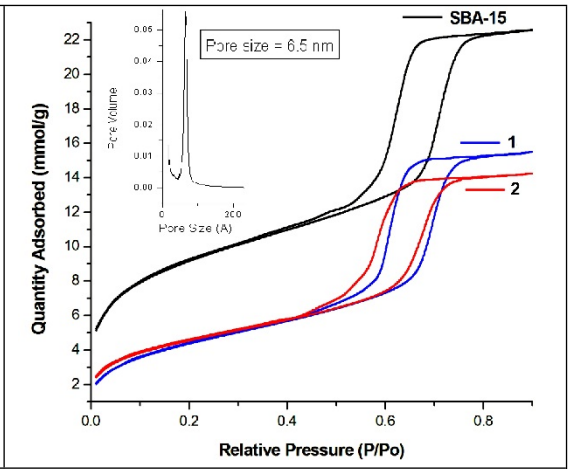

Fig. 4. Pore size distribution curve of SBA-15-supported Pd-catalyst **2**

Table 1. Structural characteristics of SBA-15-supported Pd-catalyst **2**

Sample	Surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)	Loading amount (mmol/g)
SBA-15	750	8.33	0.83	-
1	591	7.73	0.55	0.4
2	465	6.50	0.38	0.16

Diphenylacetylene 3a [1]: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.52-7.47 (m, 4H), 7.35-7.28 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 131.5, 128.1, 128.1, 123.2, 89.6. EI-MS *m/z* = 178 (M^+).

Phenyl-p-tolyacetylene 3b [2]: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.51-7.49 (m, 2 H), 7.42 (d, *J* = 7.89 Hz, 2 H), 7.32-7.26 (m, 3 H), 7.12 (d, *J* = 7.88 Hz, 2 H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 138.2, 131.4, 129.2, 128.3, 128.3, 123.4, 120.3, 89.7, 88.6, 21.5. EI-MS *m/z* = 192 (M^+).

4-Methoxyphenyl-phenylacetylene 3c [3]: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.51-7.47 (m, 4 H), 7.35-7.31 (m, 3 H), 6.85 (dd, *J* = 8.78, 2.2 Hz, 2 H), 3.83 (s, 3 H).^{13}C NMR ($CDCl_3$, 125 MHz) δ: 159.3, 133.2, 131.2, 128.4, 127.8, 123.6, 115.4, 114.0, 89.4, 88.1, 55.2. EI-MS *m/z* = 208 (M^+).

4-Acetylphenyl-phenylacetylene 3d [4]: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.92 (d, *J* = 8.49Hz, 2 H), 7.60 (d, *J* = 8.49 Hz, 2 H), 7.55-7.53 (m, 2H), 7.37-7.34 (m, 3 H), 2.59 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 197.2, 136.3, 131.9, 131.7, 128.9, 128.6, 128.1, 128.1, 122.5, 92.8, 88.4, 26.7. EI-MS *m/z* = 220 (M^+).

4-Cyanophenyl-phenylacetylene 3e [5]: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.66-7.59 (m, 4 H), 7.57-7.54 (m, 2 H), 7.41-7.38 (m, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 132.1, 131.7, 129.2, 128.6, 128.3, 122.3, 118.6, 111.5, 93.8, 87.8. EI-MS *m/z* = 203 (M^+).

4-Nitrophenyl-phenylacetylene 3f [6]: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.20 (d, *J* = 8.92 Hz, 2 H), 7.65 (d, *J* = 8.90 Hz, 2 H), 7.57-7.54 (m, 2 H), 7.41-7.37 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ:

147.1, 132.1, 131.9, 130.3, 129.3, 128.6, 123.8, 122.1, 94.8, 87.6. EI-MS *m/z* = 223 (M^+).

4-Trifluoromethylphenyl-phenylacetylene 3g [7]: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.64-7.61 (m, 4 H), 7.58-7.55 (m, 2 H), 7.38-7.35 (m, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 131.9, 131.8, 130.0 (*J* = 54.66 Hz), 128.9, 128.5, 127.2 (*J* = 2.0 Hz), 125.4 (*J* = 6.16 Hz), 123.8, 122.6, 91.8, 87.7. EI-MS *m/z* = 246 (M^+).

4-Methoxybiphenyl 4a [8]: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.83 (s, 3 H), 6.97 (d, *J* = 8.6 Hz, 2 H), 7.30 (t, *J* = 8.0 Hz, 1 H), 7.42 (t, *J* = 8.0 Hz, 2 H), 7.51-7.55 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 55.2, 114.2, 126.7, 128.1, 128.2, 128.7, 133.7, 140.8, 159.1; FTIR (cm^{-1}): 3032, 3010, 2836, 1609, 1518, 1485, 1440, 1291, 1261, 1245, 1215, 1043, 833, 746, 719, 697; MS-EI, m/z 184 (M^+).

4-Methylbiphenyl 4b [9]: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.39 (s, 3 H), 7.25 (d, *J* = 8.0 Hz, 2 H), 7.31 (t, *J* = 7.4 Hz, 1 H), 7.42 (t, *J* = 7.4 Hz, 2 H), 7.49 (d, *J* = 8.0 Hz, 2 H), 7.58 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.0, 126.9, 127.0, 128.6, 129.4, 137.0, 138.3, 141.1; FTIR (cm^{-1}): 3031, 2920, 2859, 1601, 1518, 1486, 1445, 1216, 1111, 1038, 1007, 821, 746, 696; MS-EI, m/z 168 (M^+).

Biphenyl-4-ol 4c [9]: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.96 (brs, 1 H), 6.62 (d, *J* = 8.6 Hz, 2 H), 6.91 (d, *J* = 8.6 Hz, 1 H), 7.30 (t, *J* = 7.4 Hz, 1 H), 7.41 (t, *J* = 7.4 Hz, 1 H), 7.47-7.54 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 115.6, 126.6, 128.3, 128.7, 134.0, 140.7, 155.3; FTIR (cm^{-1}): 3362, 3019, 1582, 1485, 1257, 1213, 1171, 1006, 822, 742, 698, 667; MS-EI, m/z 170 (M^+).

Biphenyl-4-amine 4d [10]: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.66 (brs, 2 H), 6.45 (d, *J* = 8.6 Hz, 2 H), 6.75 (d, *J* = 8.6 Hz, 1 H), 7.26 (t, *J* = 7.4 Hz, 1 H), 7.37-7.42 (m, 4 H), 7.52 (d, *J* = 7.4 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 115.3, 117.2, 126.3, 127.9, 128.6, 131.5, 135.4, 137.8, 141.0, 145.9; FTIR (cm^{-1}): 3452, 3368, 3215, 3025, 2922, 1617, 1588, 1484, 1297, 1177, 1058, 1000, 814, 751, 689; MS-EI, m/z 169 (M^+).

4,4'-dimethylbiphenyl 4e [9]: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.38 (s, 6 H), 7.23 (dd, *J* = 8.0, 1.7 Hz, 4 H), 7.47 (dd, *J* = 8.0, 1.7 Hz, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.0, 126.7, 129.4,

136.6, 138.2; FTIR (cm^{-1}): 3032, 2924, 2854, 1500, 1214, 1111, 1002, 803, 746, 668; MS-EI, m/z 182 (M^+).

4-Acetyl- 1,1'-biphenyl 4f [11]: ^1H NMR (500 MHz, $CDCl_3$) δ = 2.64 (s, 3 H), 7.47 (t, *J* = 7.4, Hz, 2 H), 7.62-7.69 (m, 5 H), 8.04 (d, *J* = 8.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl^3$) δ = 26.6, 127.2, 128.1, 128.9, 129.7, 135.8, 137.9, 139.8, 145.7, 197.7; FTIR (cm^{-1}): 3073, 3001, 1676, 1591, 1485, 1391, 1357, 1262, 1179, 1076, 1005, 958, 835, 754, 690; MS-EI, m/z 196 (M^+).

Biphenyl-4-carbonitrile 4g [9]: ^1H NMR (500 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 7.4 Hz, 1 H), 7.48 (t, *J* = 8.5 Hz, 2 H), 7.59 (d, *J* = 7.4 Hz, 2 H), 7.69 (d, *J* = 8.6 Hz, 2 H), 7.73 (d, *J* = 8.6 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 110.9, 118.9, 127.2, 127.7, 128.6, 129.0, 132.5, 139.1, 145.6; FTIR (cm^{-1}): 3019, 2227, 1607, 1485, 1407, 1215, 1179, 1008, 842, 742, 722, 696; MS-EI, m/z 179 (M^+).

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