Supplementary Materials: Reduction of Nitroarenes into Aryl Amines and N-Aryl hydroxylamines via Activation of NaBH₄ and Ammonia-Borane Complexes by Ag/TiO₂ Catalyst

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Table S1. Textural properties of mesoporous TiO₂ nanoparticle assemblies (MTA) and Ag/MTA catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ag loading * (wt %)</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTA</td>
<td></td>
<td>149</td>
<td>0.27</td>
<td>7.1</td>
</tr>
<tr>
<td>2% Ag/MTA</td>
<td>2.1</td>
<td>126</td>
<td>0.23</td>
<td>7.1</td>
</tr>
<tr>
<td>3% Ag/MTA</td>
<td>2.9</td>
<td>128</td>
<td>0.23</td>
<td>5.6, 7.3</td>
</tr>
<tr>
<td>4% Ag/MTA</td>
<td>4.0</td>
<td>125</td>
<td>0.22</td>
<td>5.5, 7.4</td>
</tr>
<tr>
<td>7% Ag/MTA</td>
<td>6.8</td>
<td>119</td>
<td>0.21</td>
<td>5.4, 7.4</td>
</tr>
</tbody>
</table>

* Weight percent of Ag loading according to the Energy dispersive X-ray spectroscopy (EDS) data.

Figure S1. X-ray diffraction (XRD) patterns of mesoporous samples: (i) MTA; (ii) 2% Ag/MTA; (iii) 3% Ag/MTA; (iv) 4% Ag/MTA; and (v) 7% Ag/MTA.

Figure S2. Typical transmission electron microscopy (TEM) images of mesoporous 4% Ag/MTA sample, showing that individual AgNPs (appeared as dark spots as evidenced by high resolution TEM (HRTEM) and fast Fourier transformation (FFT) analysis (see Figure 1c in the text)) are uniformly dispersed on the surface of TiO₂.
Figure S3. $N_2$ adsorption-desorption isotherms at 77 K and the corresponding non-local density functional theory (NLDFT) pore size distributions (insets) for the mesoporous: (a) 2% Ag/MTA; (b) 3% Ag/MTA; (c) 4% Ag/MTA; and (d) 7% Ag/MTA materials.

Figure S4. Catalysts evaluation based on the relative conversions of (1) to amine or to the condensation products azo, azoxy and hydrazo arenes, after 4 h. First (red) columns correspond to the relative yield of amine (1a); second (blue) columns correspond to the summary of the relative yields of the dimeric products; and third (yellow) columns correspond to the reaction conversion based on the consumption of 1.
Figure S5. $^1$H-NMR and $^{13}$C-NMR of the crude mixture of the reduction of 6 in the presence of NH$_3$BH$_3$ catalyzed by 4% Ag/MTA.

Figure S6. Recycling study of the mesoporous 4% Ag/MTA catalyst (Experimental conditions: 0.2 mmol of p-nitrotoluene, 20 mg of catalyst, 1.2 mmol of NaBH$_4$, 2 mL of ethanol, room temperature, t = 6 h).
**Figure S7.** Kinetic plots for the nitroarenes 1, 2, 3, 4, 5, 7, 8 and 12 consumptions catalyzed by 4% Ag/MTA using NaBH₄ (4 mol-excess) as reducing agent.

**Figure S8.** Profile of the nitroarenes 1, 2, 3, 4, 5, 7, 8 and 12 consumptions catalyzed by 4% Ag/MTA using NaBH₄ (4 mol-excess) as reducing agent.
Figure S9. Hammett-type kinetic plots for the nitroarenes 1, 2, 3, 4, 5, 8 and 12 reductions catalyzed by 4% Ag/MTA using NaBH₄ as reducing agent. The values for $\sigma^+$ and $\sigma$ were taken from the textbook [1].

Figure S10. $^1$H-NMR and $^{13}$C-NMR of the crude mixture of the reduction of 2 in the presence of NaBH₄ in CD₃OD, catalyzed by 4% Ag/MTA, at initial reaction time (<1 h).
Figure S11. $^1$H-NMR and $^{13}$C-NMR of the crude mixture of the reduction of 5 in the presence of NaBH$_4$, catalyzed by 4% Ag/MTA, at initial reaction time (<0.5 h).

Figure S12. $^1$H-NMR of the crude mixture of the reduction of 9 in the presence of NaBH$_4$, catalyzed by 4% Ag/MTA, at initial reaction time (<0.5 h).

$^1$H-NMR and $^{13}$C-NMR Data

Toluidine [2,3]

$^1$H-NMR (300 MHz, CDCl$_3$): 6.91 (d, 2H, $J = 8.5$ Hz), 6.56 (d, 2H, $J = 8.5$ Hz), 3.49 (br, 2H, -NH$_2$), 2.19
(s, 3H); $^{13}$C-NMR (75 MHz, CDCl$_3$): 143.6, 129.5, 127.6, 115.1, 20.2.

4-Methoxyaniline [2]

![4-Methoxyaniline](image)

$^1$H-NMR (300 MHz, CDCl$_3$): 6.75 (d, 2H, $J = 9$ Hz), 6.65 (d, 2H, $J = 9$ Hz), 3.74 (s, 3H), 3.48 (br, 2H, -NH$_2$); $^{13}$C-NMR (75 MHz, CDCl$_3$): 152.8, 139.9, 116.4, 114.7, 55.7.

4-Bromoaniline [3]

![4-Bromoaniline](image)

$^1$H-NMR (300 MHz, CDCl$_3$): 7.22 (d, 2H, $J = 8.5$ Hz), 6.53 (d, 2H, $J = 8.5$ Hz), 3.65 (br, 2H, -NH$_2$); $^{13}$C-NMR (75 MHz, CDCl$_3$): 145.4, 132.0, 116.7, 110.2.

4-Chloroaniline [3]

![4-Chloroaniline](image)

$^1$H-NMR (300 MHz, CDCl$_3$): 7.04 (d, 2H, $J = 8.5$ Hz), 6.64 (d, 2H, $J = 8.5$ Hz), 3.62 (br, 2H, -NH$_2$); $^{13}$C-NMR (75 MHz, CDCl$_3$): 144.8, 128.9, 123.0, 116.0.

Methyl 4-aminobenzoate [4]

![Methyl 4-aminobenzoate](image)

$^1$H-NMR (300 MHz, CDCl$_3$): 7.83 (d, 2H, $J = 8.5$ Hz), 6.62 (d, 2H, $J = 8.5$ Hz), 4.09 (br, 2H, -NH$_2$), 3.84 (s, 3H); $^{13}$C-NMR (75 MHz, CDCl$_3$): 167.2, 150.8, 131.5, 119.8, 113.7, 51.5.

4-Aminophenol [3]
\[
\text{H-NMR (300 MHz, CD}_{2}\text{OD): 6.56 (d, 2H, } J = 9 \text{ Hz), 6.51 (d, 2H, } J = 9 \text{ Hz), 3.40 (br, 2H, -NH}_{2}\text{); } ^{13}\text{C-NMR (75 MHz, CD}_{2}\text{OD): 149.7, 141.7, 116.8, 116.7.}
\]

Aniline [2]

\[
\text{H-NMR: (300 MHz, CDCl}_{3}\text{): 7.13 (t, 2H, } J = 8.5 \text{ Hz), 6.73 (t, 1H, } J = 8.5 \text{ Hz), 6.65 (d, 2H, } J = 8.5 \text{ Hz), 3.42 (br, 2H, -NH}_{2}\text{); } ^{13}\text{C-NMR: (75 MHz, CDCl}_{3}\text{): 146.2, 129.0, 118.3, 114.9.}
\]

3-Aminobenzonitrile [5]

\[
\text{H-NMR (300 MHz, CDCl}_{3}\text{): 7.18 (t, 1H, } J = 7.5 \text{ Hz), 6.96 (d, 1H, } J = 7.5 \text{ Hz), 6.89 (s, 1H), 6.85 (d, 1H, } J = 7.5 \text{ Hz), 3.86 (br, 2H, -NH}_{2}\text{); } ^{13}\text{C-NMR (75 MHz, CDCl}_{3}\text{): 146.9, 129.9, 121.8, 119.2, 119.1, 117.5, 112.9.}
\]

4-Aminoaniline [2]

\[
\text{H-NMR (300 MHz, CDCl}_{3}\text{): 6.56 (s, 4H), 3.19 (br, 4H, -NH}_{2}\text{); } ^{13}\text{C-NMR (75 MHz, CDCl}_{3}\text{): 138.6, 116.7.}
\]

6-aminoisobenzofuran-1(3H)-one [6]

\[
\text{H-NMR (300 MHz, CDCl}_{3}\text{): 7.21 (d, 1H, } J = 8.0 \text{ Hz), 7.13 (d, 1H, } J = 2.0 \text{ Hz), 6.95 (dd, 1H, } J_{1} = 8.0 \text{ Hz, } J_{2} = 2.0 \text{ Hz), 5.20 (s, 2H), 3.92 (s, 2H); } ^{13}\text{C-NMR (125 MHz, CDCl}_{3}\text{): 171.4, 147.5, 136.4, 127.0, 122.7, 121.6, 109.8, 69.6.}
\]
3-Ethylaniline [2,3]

![Image of 11a](here)

$^1$H-NMR (300 MHz, CDCl$_3$): 7.07 (t, 1H, $J = 7.5$ Hz), 6.61 (d, 1H, $J = 7.5$ Hz), 6.54 (s, 1H), 6.51 (d, 1H, $J = 7.5$ Hz), 3.56 (s, 2H), 2.56 (q, 2H, $J = 7$ Hz), 1.21 (t, 3H, $J = 7$ Hz).

1-Ethyl-3-nitrobenzene

![Image of 11c](here)

$^1$H-NMR (300 MHz, CDCl$_3$): 7.76-7.72 (m, 1H), 7.43 (t, 1H, $J = 7.7$ Hz), 7.31 (d, 2H, $J = 7.7$ Hz), 2.77 (q, 2H, $J = 7.5$ Hz). 1.32 (t, 3H, $J = 7.5$ Hz).

3-amino aniline [3,4]

![Image of 12a](here)

$^1$H-NMR (500 MHz, CDCl$_3$): 6.94 (t, 1H, $J = 7.9$ Hz), 6.12 (dd, 2H, $J_1 = 7.9$ Hz, $J_2 = 2.0$ Hz), 6.04 (t, 1H, $J = 2.0$ Hz), 3.56 (br, 4H, -NH$_2$); $^{13}$C-NMR (125 MHz, CDCl$_3$): 147.5, 130.2, 106.0, 101.9.

N-(p-tolyl)hydroxylamine [7,8]

![Image of 1b](here)

$^1$H-NMR (300 MHz, CDCl$_3$): 7.09 (d, 2H, $J = 8.4$ Hz), 6.92 (d, 2H, $J = 8.4$ Hz), 2.30. $^{13}$C-NMR (75 MHz, CDCl$_3$): 147.3, 132.0, 129.5, 115.2, 20.6.

N-(4-methoxyphenyl)hydroxylamine [7,8]

![Image of 2b](here)

$^1$H-NMR (300 MHz, CD$_2$OD): 6.94 (d, 2H, $J = 9$ Hz), 6.80 (d, 2H, $J = 9$ Hz), 3.72 (s, 3H); $^{13}$C-NMR (125 MHz, CD$_2$OD): 156.5, 145.8, 118.3, 115.7, 56.1; MS m/z (ESI) calcd for C$_7$H$_9$NO$_2$ (M-H)$^-$ 138.06,
found 137.85.

N-(4-bromophenyl)hydroxylamine [7]

\[ \text{H-NMR (300 MHz, CDCl}_3\text{): 7.38 (d, 2H, } J = 8.7 \text{ Hz), 6.88 (d, 2H, } J = 8.7 \text{ Hz), 5.51 (br, 1H). C-NMR (75 MHz, CDCl}_3\text{): 148.9, 131.9, 116.2, 114.5.} \]

N-(4-chlorophenyl)hydroxylamine [7]

\[ \text{H-NMR (300 MHz, CDCl}_3\text{): 7.24 (d, 2H, } J = 8.8 \text{ Hz), 6.93(d, 2H, } J = 8.8 \text{ Hz). C-NMR (75 MHz, CDCl}_3\text{): 148.3, 128.9, 127.2, 115.9. H-NMR (500 MHz, CD}_3\text{OD): 7.17 (d, 2H, } J = 8.5 \text{ Hz), 6.93 (d, 2H, } J = 8.5 \text{ Hz); C-NMR (125 MHz, CD}_3\text{OD): 151.8, 129.5, 126.2, 116.2. MS m/z (ESI) calcd for C}_8\text{H}_9\text{NOCl (M-H)}^+ \text{ 142.56, found 142.41.}} \]

Methyl 4-(hydroxyamino)benzoate [7]

\[ \text{H-NMR (300 MHz, CDCl}_3\text{): 7.96 (d, 2H, } J = 8.4 \text{ Hz), 6.98 (d, 2H, } J = 8.4 \text{ Hz), 3.88. C-NMR (75 MHz, CDCl}_3\text{): 167.0, 154.0, 131.0, 123.5, 113.0, 51.8. H-NMR (300 MHz, CD}_3\text{OD): 7.85 (d, 2H, } J = 8.5 \text{ Hz), 6.93 (d, 2H, } J = 8.5 \text{ Hz), 3.87 (s, 3H). MS m/z (ESI) calcd for C}_8\text{H}_9\text{NO}_3\text{ (M-H)}^+ \text{ 166.05, found 165.90.}} \]

N-phenylhydroxylamine [7]

\[ \text{H-NMR (300 MHz, CDCl}_3\text{): 7.31–7.28 (m, 2H), 7.02–6.97 (m, 3H). C-NMR (75 MHz, CDCl}_3\text{): 149.7, 128.9, 122.4, 114.8.} \]

3-(Hydroxyamino)benzonitrile [7,8]
\[ \text{Nanomaterials 2016, 6, 54} \]

\[ \begin{align*}
\text{H-NMR (500 MHz, CDCl}_3\text{): } & 7.34 \ (t, \ 1H, \ J = 8.0 \text{ Hz}), \ 7.29 \ (s, \ 1H), \ 7.23 \ (d, \ 1H, \ J = 8.0 \text{ Hz}), \ 7.15 \ (d, \ 1H, \ J = 8.0 \text{ Hz}). \ \text{\textsuperscript{13}C-NMR (125 MHz, CDCl}_3\text{): } 150.4, \ 129.6, \ 125.5, \ 118.9, \ 118.3, \ 117.1, \ 112.7. \ MS \ m/z \ (\text{ESI}) \text{ calcd for C}_7\text{H}_6\text{N}_2\text{O} \ (\text{M-H})^+ \ 133.04, \ \text{found } 132.95.
\end{align*} \]

N-(4-nitrophenyl)hydroxylamine [7]

\[ \begin{align*}
\text{H-NMR (300 MHz, Acetone-d}_6\text{): } & 8.11 \ (d, \ 2H, \ J = 9.2 \text{ Hz}), \ 7.03 \ (d, \ 2H, \ J = 9.2 \text{ Hz}). \ \text{\textsuperscript{13}C-NMR (75 MHz, Acetone-d}_6\text{): } 157.9, \ 140.7, \ 126.0, \ 112.0.
\end{align*} \]

6-(hydroxyamino)isobenzofuran-1(3H)-one [7,8]

\[ \begin{align*}
\text{H-NMR (500 MHz, Acetone-d}_6\text{): } & 8.15 \ (br, \ 1H), \ 7.46 \ (d, \ 1H, \ J = 8.3 \text{ Hz}), \ 7.39 \ (s, \ 1H, \ J = 2.0 \text{ Hz}), \ 7.31 \ (dd, \ 1H, \ J_1 = 8.3 \text{ Hz}, \ J_2 = 1.7 \text{ Hz}), \ 5.27 \ (s, \ 2H). \ \text{\textsuperscript{13}C-NMR (125 MHz, Acetone-d}_6\text{): } 171.7, \ 148.6, \ 139.7, \ 127.2, \ 123.5, \ 120.9, \ 108.7, \ 70.3.
\end{align*} \]

N-(3-Vinylphenyl)hydroxylamine [7]

\[ \begin{align*}
\text{H-NMR (500 MHz, CD}_3\text{OD): } & 7.16 \ (t, \ 1H, \ J = 7.5 \text{ Hz}), \ 7.05 \ (s, \ 1H), \ 6.93 \ (d, \ 1H, \ J = 7.5 \text{ Hz}), \ 6.84 \ (d, \ 1H, \ J = 7.5 \text{ Hz}), \ 6.67 \ (dd, \ 1H, \ J_1 = 18 \text{ Hz}, \ J_2 = 12 \text{ Hz}), \ 5.69 \ (d, \ 1H, \ J = 18 \text{ Hz}), \ 5.15 \ (d, \ 1H, \ J = 12 \text{ Hz}); \ \text{\textsuperscript{13}C-NMR (125 MHz, CD}_3\text{OD): } 153.0, \ 139.8, \ 138.6, \ 130.2, \ 120.2, \ 116.4, \ 114.2, \ 113.3; \ MS \ m/z \ (\text{ESI}) \text{ calcd for C}_8\text{H}_9\text{NO} \ (\text{M-H})^+ \ 134.06, \ \text{found } 133.95.
\end{align*} \]

3-N-hydroxyl-aniline [7,8]
$^1$H-NMR (500 MHz, CDCl$_3$): 7.04 (t, 1H, $J$ = 8.0 Hz), 6.38 (s, 1H), 6.36 (d, 1H, $J$ = 8.0 Hz), 6.31 (d, $J$ = 8.0 Hz); $^{13}$C-NMR (125 MHz, CDCl$_3$): 151.0, 147.2, 129.8, 109.2, 104.9, 101.4

$^1$H-NMR and $^{13}$C-NMR Spectra
References


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