Supplementary Information

Room temperature complete reduction of nitroarenes over novel Cu/SiO$_2$@NiFe$_2$O$_4$ nano-catalyst in aqueous medium – A kinetic and mechanistic study

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Fig. S1. ED indexing of NiFe$_2$O$_4$. 
Supplementary Information

EDS data

Spectrum processing:
Peak possibly omitted: 0.271 keV

Processing option: All elements analyzed (Normalised)
Number of iterations = 3
Standard:
- O SiO2 1-Jun-1999 12:00 AM
- Si SiO2 1-Jun-1999 12:00 AM
- Fe Fe 1-Jun-1999 12:00 AM
- Ni Ni 1-Jun-1999 12:00 AM
- Cu Cu 1-Jun-1999 12:00 AM

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>32.91</td>
<td>61.19</td>
</tr>
<tr>
<td>Si K</td>
<td>8.20</td>
<td>8.68</td>
</tr>
<tr>
<td>Fe K</td>
<td>29.85</td>
<td>15.90</td>
</tr>
<tr>
<td>Ni K</td>
<td>16.35</td>
<td>8.28</td>
</tr>
<tr>
<td>Cu L</td>
<td>12.69</td>
<td>5.94</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>
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Elemental Mapping

The elemental mapping data showing uniform distribution of Si and Cu on the support.
Supplementary Information

XPS of individual elements

Fig. S2. XPS spectrum showing C 1s peak calibrated to 284.6eV. Remaining spectra are of individual elements present in the active catalyst sample Cu/SiO$_2$@NiFe$_2$O$_4$. Starting from left C 1s, O 1s, Fe 2p, Ni 2p.

VSM

Table S1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ms (emu/g)</th>
<th>Mr (emu/g)</th>
<th>Hc (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/SiO$_2$@NiFe$_2$O$_4$</td>
<td>22.1165</td>
<td>2.6510</td>
<td>232</td>
</tr>
<tr>
<td>SiO$_2$@NiFe$_2$O$_4$</td>
<td>24.4882</td>
<td>2.3524</td>
<td>200</td>
</tr>
<tr>
<td>NiFe$_2$O$_4$</td>
<td>28.7444</td>
<td>2.5489</td>
<td>132</td>
</tr>
</tbody>
</table>

Ms- Saturation Magnetization
Mr- Remanent Magnetization
Hc - Coercivity

As expected the saturation magnetisation (Ms) was highest for NiFe$_2$O$_4$ which decreased after silica coating and was found lowest for Cu/SiO$_2$@NiFe$_2$O$_4$ as seen in the fig. S6.
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Product characterisation

Fig. S3. $^1$H NMR spectrum of the isolated product when performed on 1 mmol scale matches with reference ¹.

Reference

Supplementary Information

Fig. S4. Plot of $k$ at different temperatures.

Table S2
Recyclability of the catalyst

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Time (min) for total conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>7</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>7</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
<td>11</td>
</tr>
<tr>
<td>4&lt;sup&gt;th&lt;/sup&gt;</td>
<td>14</td>
</tr>
<tr>
<td>5&lt;sup&gt;th&lt;/sup&gt;</td>
<td>20</td>
</tr>
</tbody>
</table>

Table S3
Solvent Studies using Nitrobenzene (0.5 mmol), Catalyst (6 mg), NaBH4 (2.5 mmol)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent system</th>
<th>Observations*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>THF</td>
<td>no desired product</td>
</tr>
<tr>
<td>2</td>
<td>Acetonitrile</td>
<td>no desired product</td>
</tr>
<tr>
<td>3</td>
<td>Methanol</td>
<td>3.5h for complete conversion</td>
</tr>
<tr>
<td>4</td>
<td>Ethanol</td>
<td>5h for complete conversion</td>
</tr>
<tr>
<td>5</td>
<td>Water</td>
<td>2.5h for complete conversion</td>
</tr>
<tr>
<td>6</td>
<td>1:1 Water-THF</td>
<td>8h for complete conversion</td>
</tr>
<tr>
<td>7</td>
<td>1:1 Water-Acetonitrile</td>
<td>Multiple spots even after 5h</td>
</tr>
<tr>
<td>8</td>
<td>1:1 Water-Ethanol</td>
<td>Over 7h for complete conversion</td>
</tr>
<tr>
<td>9</td>
<td>1:1 Water-Methanol</td>
<td>2h for complete conversion</td>
</tr>
</tbody>
</table>

* Reactions were monitored on TLC.
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GC CHROMATOGRAMS

Fig. S5. A representative GC chromatogram showing Rt values of reactant Nitrobenzene, product aniline, and two intermediates Nitrosobenzene and Azobenzene.

All the GC runs were carried out using Ovi 101 column and same sequencer settings.

The above chromatograph displays the probable components of Nitrobenzene reduction. Authentic samples were injected individually to determine the retention time of the components with the set program. The subsequent chromatographs show the progress of the reaction with time in presence of Cu/SiO$_2$@NiFe$_2$O$_4$.

*NOTE: Since the boiling point of aniline (179ºC) and the internal standard used n-decane (174 ºC) are very closed and it couldn’t be well resolved at the set program, internal standard wasn’t used while performing the mechanistic studies.
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Mechanistic Study using Nitrobenzene as substrate over time
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Sample Name: Sample1
Detector: FID
System: GC
Run Date: 8/5/2016

Analysis Type: Percent Method
Time: 6:21:29 PM
Chan No: Chan 2

Peak Width | Peak Threshold | Area Reject | Height Reject
-----------|----------------|-------------|----------------
16          | 60             | 500         | 60

Reaction at 60 min

Sample Name: Sample1
Detector: FID
System: GC
Run Date: 8/5/2016

Analysis Type: Percent Method
Time: 6:34:37 PM
Chan No: Chan 2

Peak Width | Peak Threshold | Area Reject | Height Reject
-----------|----------------|-------------|----------------
16          | 60             | 500         | 60

Reaction at 75 min

Sample Name: Sample1
Detector: FID
System: GC
Run Date: 8/5/2016

Analysis Type: Percent Method
Time: 6:49:15 PM
Chan No: Chan 2

Peak Width | Peak Threshold | Area Reject | Height Reject
-----------|----------------|-------------|----------------
16          | 60             | 500         | 60

Reaction at 90 min