Supporting information for

Fe$_2$O$_3$/NGr@C- and Co-Co$_3$O$_4$/NGr@C-catalysed hydrogenation of nitroarenes under mild conditions

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1. General aspects

All the reactions and manipulations were carried out under air. As the only exception, Fe(OAc)$_2$ was stored under Ar atmosphere. All the employed chemicals were purchased by Sigma Aldrich, Alfa Aesar or Tokyo Chemical Industry. Vulcan® XC 72R carbon was purchased by Cabot Corporation (CAS No. 1333-86-4). Regarding the substrate scope, all the final products were calibrated by using commercially-available chemicals. Calibration curves were obtained using $n$-hexadecane and AcOEt as the internal standard and solvent respectively.

2. Catalysts preparation

2.1. General procedure scheme

\[
\text{Co(OAc)$_2$·4H$_2$O or Fe(OAc)$_2$} \quad + \quad \text{Phen} \quad \xrightarrow{\text{EtOH, 60 °C, in situ}} \quad \text{[Co(phen)$_2$](OAc)$_2$ or [Fe(phen)$_3$](OAc)$_2$}} \quad \xrightarrow{\text{Pyrolysis, 800 °C, 2 h, Ar}} \quad \text{Vulcan XC 72 R Adsorbed Co and Fe chelates (inactive materials)}}
\]

Figure S1. General procedure scheme for the preparation of the catalysts.

2.2. Co-Co$_3$O$_4$/NGr@C$^{[1]}$

In order to obtain 1 g of the final catalytically active material, 124 mg of Co(OAc)$_2$·4H$_2$O were dissolved in 20 mL of absolute ethanol. Then, 180 mg of Phen were added and the so-obtained brown solution was stirred at 60 °C for 2 hours. Subsequently, Vulcan® XC 72R carbon (696 mg) was portionwise added. The suspension was maintained under stirring for 18 h. Then, ethanol was carefully removed by rotary evaporation and the solid material was dried for 4 hours under vacuum. The sample was finally subjected to pyrolysis (see Section 2.4). For scaled-up preparation see reference [1]. By using the same procedure, catalyst without the addition of Phen was prepared (named Co$_x$O$_y$@C in the text).

Elemental analyses for both the Co-based catalysts were the following:

**Table S1. Elemental analyses of Co-based catalysts.**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-Co$_3$O$_4$/NGr@C</td>
<td>92.18</td>
<td>0.18</td>
<td>2.61</td>
<td>3.05</td>
</tr>
<tr>
<td>Co$_y$O$_x$@C</td>
<td>83.10</td>
<td>0.18</td>
<td>&lt;0.1</td>
<td>4.33</td>
</tr>
</tbody>
</table>

The obtained results are in accordance within experimental error to those reported in reference [2]:

C: 92.28; H: 0.20; N: 2.70
2.3. Fe$_2$O$_3$/NGr@C

In order to obtain 1 g of the final catalytic active material, 94 mg of Fe(OAc)$_2$ (0.5 mmol) were dissolved in 20 mL of absolute ethanol. Then, 291 mg of Phen (1.5 mmol, 3 equivalents with respect to Fe acetate) were added and the so-obtained brown solution was stirred at 60 °C for 2 hours. Subsequently, Vulcan® XC 72R carbon was portionwise added (615 mg). The suspension was maintained under stirring for 18 h. Then, ethanol was carefully removed by rotary evaporation and the solid material was dried for 4 hours under vacuum. The sample was finally subjected to pyrolysis (see Section 2.4). For scaled-up preparation see reference [2]. By using the same procedure, catalyst without the addition of Phen was prepared (titled Fe$_x$O$_y$@C in the text).

Elemental analyses for both the Fe-based catalysts were the following

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$/NGr@C</td>
<td>90.94</td>
<td>0.28</td>
<td>2.79</td>
<td>2.95</td>
</tr>
<tr>
<td>Fe$_x$O$_y$@C</td>
<td>82.03</td>
<td>0.096</td>
<td>&lt;0.1</td>
<td>4.53</td>
</tr>
</tbody>
</table>

The obtained results are in accordance within experimental error to those reported in reference [4]:

C: 91.10; H: 0.19; N: 2.69

2.4. Pyrolysis procedure (for both the catalysts)

The solid obtained as previously described was transferred into a crucible equipped with lid and placed in the pyrolysis chamber of AUSTROMAT 264 pyrolytic oven. The oven was heated to 100 °C (25 K/min) flushing 10 mL·min$^{-1}$ of Ar. Once the temperature reached 100 °C, the chamber was evacuated for 5 min and flood with Ar for 60 °C. The latter operation was repeated for two times. Thus, the temperature was increased to 800 °C and maintained for 2 h. During the whole process Ar was flushed. At the end, the heating was stopped and the chamber allowed cooling down to room temperature. The lid containing the active catalyst was removed. Both the catalysts can be stored under air for months without loss of activity.

3. Procedures for catalytic and recycling experiments

3.1. Standard catalytic experiments

In an 8 mL vial fitted with magnetic stirring bar and septum cap, nitroarene (0.5 mmol), catalyst, internal standard ($n$-hexadecane) and the solvent were added. The, additives were added if stated. A needle was inserted in the septum which allows gaseous reagents to enter. The vials (up to seven) were placed into a 300 mL steel Parr autoclave. The autoclave was flushed with hydrogen twice at 20 bar and finally pressurized to the desired value. Then it was placed into an aluminium block pre-heated to the desired temperature. At the end of the reaction, the autoclave was quickly cooled down at room temperature with an ice bath and vented. Finally, the samples were removed from the autoclave, diluted with AcOEt, filtered using a Pasteur pipette filled with celite (6 cm pad) and analysed at the GC.

3.2. Recycling experiments
For the catalyst recycling experiments, 6-fold scaled up reaction were carried out. All the reactions were performed in glass vials according previously described procedure. After completion of the reaction, the content of the vial was quantitatively transferred into a centrifuge tube. The reaction mixture was centrifuged and the catalyst was separated by the supernatant. The latter procedure was repeated for three times, washing the catalysts with EtOH. Then the catalyst was dried under vacuum overnight. The dried material was so used for the next catalytic reaction.

After the fifth recycle, both the materials were subjected to elemental analysis. The obtained results are following reported:

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-Co₃O₄/NGr@C</td>
<td>92.01</td>
<td>0.25</td>
<td>2.59</td>
</tr>
<tr>
<td>Fe₃O₄/NGr@C</td>
<td>91.01</td>
<td>0.23</td>
<td>2.77</td>
</tr>
</tbody>
</table>
4. Catalysts characterisation

4.1. XRD pattern

Figura S2. XRD patterns for Co-Co\textsubscript{3}O\textsubscript{4}/NGr@C (A) and Fe\textsubscript{2}O\textsubscript{3}/NGr@C.

XRD diffraction patterns are consistent with those previously reported (see references [5] and [6] for Fe\textsubscript{2}O\textsubscript{3}/NGr@C and Co-Co\textsubscript{3}O\textsubscript{4}/NGr@C, respectively). In the case of Fe\textsubscript{2}O\textsubscript{3}/NGr@C, the presence of iron oxides is confirmed but hardly seen through the overlapping of the characteristic peaks in a range of 2θ form 42° to 50°.
4.2. TEM images

Figure S3. TEM images of Co-Co$_3$O$_4$/NGr@C: survey of the material (A) and graphene structures (B, C, D) around the metal NPs.
Figura S4. TEM images of Fe$_2$O$_3$/NGr@C: survey of the material (A) and graphene structures (B, C, D) around the metal NPs.

TEM images are consistent with those previously reported (see references [2], [6] and [4], [5] for Co-Co$_3$O$_4$/NGr@C and Fe$_2$O$_3$/NGr@C, respectively).
5. Solvent screening

5.1. Co-Co₃O₄/NGr@C

Figure S5. Solvent screening for Co-Co₃O₄/NGr@C. Reaction conditions: 0.5 mol % Co-Co₃O₄/NGr@C (5 mg), 0.5 mmol PhNO₂, 70 °C, 20 bar H₂, 13 h, solvent = 2 mL (+ 100 μL H₂O if stated)

5.2. Fe₂O₃/NGr@C

Figure S6. Solvent screening for Fe₂O₃/NGr@C. Reaction conditions: 4.5 mol % Fe₂O₃/NGr@C (42 mg), 0.5 mmol PhNO₂, 120 °C, 50 bar H₂, 4 h, solvent = 3 mL (in the case of solvent-water systems, their ratio was 1:1)
Figure S7. Screening of water amount for Fe$_2$O$_3$/NGr@C. Reaction conditions: 4.5 mol % Fe$_2$O$_3$/NGr@C, 0.5 mmol PhNO$_2$, 120 °C, 50 bar H$_2$, 4 h, solvent = 3 mL (total).
6. Inorganic bases screening

6.1. Co-Co$_3$O$_4$/NGr@C

Figure S8. Inorganic bases screening for Co-Co$_3$O$_4$/NGr@C. Reaction conditions: 0.5 mmol PhNO$_2$, 0.5 mol % Co Co-Co$_3$O$_4$/NGr@C (5 mg), 70 °C, 20 bar H$_2$, 13 h, solvent: 2 mL EtOH + 100 μL H$_2$O, base: 1 equiv. with respect to the PhNO$_2$.

6.2. Fe$_2$O$_3$/NGr@C

Figure S9. Inorganic bases screening for Fe$_2$O$_3$/NGr@C. Reaction conditions: 0.5 mmol PhNO$_2$, 4.5 mol % Fe$_2$O$_3$/NGr@C (42 mg), 120 °C, 50 bar H$_2$, 4 h, solvent: 3 mL MeOH, base: 1 equiv. with respect to the PhNO$_2$. 
7. Acids screening

7.1. Co-Co$_3$O$_4$/NGr@C

![Graph](image)

Figure S10. Acids screening for Co-Co$_3$O$_4$/NGr@C. Reaction conditions: 0.5 mmol PhNO$_2$, 0.5 mol % Co Co-Co$_3$O$_4$/NGr@C (5 mg), 70 °C, 20 bar H$_2$, 13 h, solvent: 2 mL EtOH + 100 μL H$_2$O, acid: 1 equiv. with respect to the PhNO$_2$.

7.2. Fe$_2$O$_3$/NGr@C

![Graph](image)

Figure S11. Acids screening for Fe$_2$O$_3$/NGr@C. Reaction conditions: 0.5 mmol PhNO$_2$, 4.5 mol % Fe$_2$O$_3$/NGr@C (42 mg), 120 °C, 50 bar H$_2$, 4 h, solvent: 3 mL MeOH, acid: 1 equiv. with respect to the PhNO$_2$. 

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8. Optimization of the base amount

8.1. Co-Co$_3$O$_4$/NGr@C

Figure S12. Optimization of the Et$_3$N amount for Co-Co$_3$O$_4$/NGr@C. Reaction conditions: 0.5 mmol PhNO$_2$, 0.5 mol % Co-Co$_3$O$_4$/NGr@C (5 mg), 70 °C, 20 bar H$_2$, 13 h, solvent: 2 mL EtOH + 100 μL H$_2$O.

8.2. Fe$_2$O$_3$/NGr@C

Figure S13. Optimisation of the NH$_3$ amount for Fe$_2$O$_3$/NGr@C. Reaction conditions: 0.5 mmol PhNO$_2$, 4.5 mol % Fe$_2$O$_3$/NGr@C (42 mg), 120 °C, 50 bar H$_2$, 4 h, solvent: 3 mL EtOH.
9. Control experiments

9.1. Co-Co$_3$O$_4$/NGr@C

Table S3. Co-catalysed hydrogenation of nitrobenzene to aniline: control experiments.$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion [%]$^b$</th>
<th>Selectivity [%]$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5 mol % Co$_x$O$_y$@C</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>2$^c$</td>
<td>0.5 mol % Co$_x$O$_y$@C</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>3$^d$</td>
<td>0.5 mol % Co-Co$_3$O$_4$/NGr@C</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>4$^{c,d}$</td>
<td>0.5 mol % Co-Co$_3$O$_4$/NGr@C</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>6$^e$</td>
<td>-</td>
<td>&lt;1</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: 0.5 mmol PhNO$_2$; solvent = 2 mL EtOH + 100 µL H$_2$O; $^b$ GC values using $n$-hexadecane as the internal standard; $^c$ 1 equiv. of Et$_3$N was added; $^d$ Reaction carried out under 20 bar of N$_2$.

9.2. Fe$_2$O$_3$/NGr@C

Table S4. Fe-catalysed hydrogenation of nitrobenzene to aniline: control experiments.$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion [%]$^b$</th>
<th>Selectivity [%]$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.5 mol % Fe$_x$O$_y$@C</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>2$^c$</td>
<td>4.5 mol % Fe$_x$O$_y$@C</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>3$^e$</td>
<td>4.5 mol % Fe$_x$O$_y$@C</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>4$^d$</td>
<td>4.5 mol % Fe$_2$O$_3$/NGr@C</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>5$^{c,d}$</td>
<td>4.5 mol % Fe$_2$O$_3$/NGr@C</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>6$^{c,d}$</td>
<td>4.5 mol % Fe$_2$O$_3$/NGr@C</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>8$^e$</td>
<td>-</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>9$^e$</td>
<td>-</td>
<td>&lt;1</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: 0.5 mmol PhNO$_2$; 3 mL MeOH; $^b$ GC values using $n$-hexadecane as internal standard; $^c$ 1 equiv. of NH$_3$ was added; $^d$ Reaction carried out under 20 bar of N$_2$; $^e$ 1 equiv. of DMAP (4-dimethylaminopyridine) was added.
The hot filtration test was carried out following the standard procedure for a catalytic experiment. The reaction was stopped before complete conversion. A small amount of the vial contents was filtered by using Pasteur pipette filled with celite and an aliquot of the filtrate analysed at GC. Then, the remaining reaction mixture was quantitatively transferred into a Schlenk flask and heated up to 90 °C for 1 hour. The reaction mixture was filtered while hot and the filtrate was transferred into a clean reaction vial and subsequently subjected to the standard reaction conditions for 13 h.

Table S5. Maitlis’ hot filtration test.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion before filtration [%][c]</th>
<th>Conversion after filtration [%][c,d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Co-Co₃O₄/NGr@Cᵃ</td>
<td>52.3</td>
<td>53.0</td>
</tr>
<tr>
<td>2</td>
<td>Fe₂O₃/NGr@Cᵇ</td>
<td>38.5</td>
<td>37.8</td>
</tr>
</tbody>
</table>

ᵃ Reaction conditions for Co-Co₃O₄/NGr@C: 0.5 mmol PhNO₂, 0.5 mol % Co-Co₃O₄/NGr@C (5 mg), 70 °C, 20 bar H₂, solvent: 2 mL EtOH + 100 µL H₂O, 1 equiv. Et₃N; ᵇ Reaction conditions for Fe₂O₃/NGr@C: 0.5 mmol PhNO₂, 4.5 mol % Fe₂O₃/NGr@C (42 mg), 120 °C, 50 bar H₂, solvent: 3 mL MeOH, 1 equiv. NH₃; c Conversion determined by GC using n-hexadecane as internal standard; d After 13 h of reaction in the same reaction conditions.
11. MS spectra of side-products detected in the catalytic run employing In as substrate, Co-Co₃O₆/NGr@C as catalyst and 1 equiv. of Et₃N as additive.

Figure S14. MS spectra of diethyl-5-aminoisophthalate.

Figure S15. MS spectra of 1-methyl-3-ethyl-5-aminoisophthalate.

12. References


