Supporting Information
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SUPPORTING INFORMATION

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1. Preparation of Catalysts.

Vulcan XC72R-supported metal-based and intermetallic nickel-silicide materials were prepared by the impregnation method as previously reported:

Fe$_2$O$_3$/NGr@C, CoCo$_3$O$_4$/NGr@C, NiNiO/NGr@C, NiSi/NiO-SiO$_2$@SiO$_2$.

Preparation of the Fe$_2$O$_3$/NGr@C*-catalyst.

Vulcan XC72R-supported iron-based materials were prepared by the impregnation method as previously reported. A 250 mL oven-dried single-necked round-bottomed flask equipped with a Allihn reflux condenser and a Teflon-coated, egg-shaped magnetic stir bar (40 × 18 mm) was charged with Fe(OAc)$_2$ (260 mg, 1.5 mmol, 1.0 equiv.), 1,10-phenanthroline monohydrate (564 mg, 3.0 mmol, 2.0 equiv.) and dissolved in ethanol (60 mL). After stirring for 5 min at 25°C, the flask was immersed in an oil bath and heated at 60°C for 2 h. To the reaction mixture 2.10 g of carbon (Vulcan XC72R) was added via a glass funnel and the resulting heterogeneous mixture was stirred at 750 rpm for 2 h at 60°C. The flask was taken out from the bath and cooled to ambient temperature. The solvent was removed in vacuo (180 mbar, bath temperature 40°C, 200 rpm), then dried under oil pump vacuum (1.0 mmHg, 23°C) overnight. The sample was ground to a fine powder which was then transferred to a ceramic crucible (height – 20 mm, top Ø – 40 mm) and placed in an oven. The latter was evacuated to ca. 5 mbar and then flushed with argon three times. The furnace was heated to 1000°C at a rate of 25°C per minute and held at 1000°C for 2 h under argon atmosphere. After the heating was switched off the oven was allowed to reach room temperature, giving the Fe$_2$O$_3$/NGr@C* as a black powder. (Note: during the whole process argon was constantly passed through the oven).

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2. General procedure for hydrogenations.

Hydrogenation experiments on 0.5 mmol scale were carried out in 300 mL autoclave (PARR Instrument Company) in 8-mL glass vials, which were placed inside the autoclave:

An 8 mL glass vial (Ø – 14 mm, height 50 mm) equipped with a Teflon-coated oval magnetic stirring bar (8 × 5 mm) and a plastic screw cap was charged with corresponding nitroarene (0.5 mmol, 1.0 equiv.), 50 mg of Fe$_2$O$_3$/NGr@C catalyst (4.0 mol% Fe), triethylamine (70 µ, 0.5 mmol, 1.0 equiv) 2 mL THF and 0.2 mL of deionized water. The silicone septum was punctured with a 26 gauge syringe needle (0.45 × 12 mm) and the vial was placed in an aluminum plate which was then transferred into the 300 mL autoclave. Once sealed, the autoclave was placed into an aluminum block and purged 3 times with CO (at 5-10 bar). Then it was pressurized with CO to 30 bar, followed by additional 20 bar of N$_2$. The aluminum block was heated up to 125°C under thorough stirring (700 rpm). After 24 h, the autoclave was removed from the aluminum block and cooled to room temperature in a water bath. The remaining gases were discharged and the vials containing reaction products were removed from the autoclave. The reaction mixture was filtered through a Celite pad (~1 cm), concentrated and analyzed by GC and NMR.

Hydrogenation of 2s on 5.0 mmol scale:

A 25 mL autoclave (PARR Instrument Company) equipped with turbine type impeller was charged with 2s (1.30 g, 5.0 mmol, 1.0 equiv.), 500 mg of Fe$_2$O$_3$/NGr@C catalyst (4.0 mol% Fe), triethylamine (700 µ, 5.0 mmol, 1.0 equiv), 10 mL THF and 1.0 mL of deionized water. Once sealed, the autoclave was placed into an aluminum block and purged 3 times with CO (at 5-10 bar). Then it was pressurized with CO to 30 bar, followed by additional 20 bar of N$_2$. The aluminum block was heated up to 125°C under thorough stirring (400 rpm). After 24 h, the autoclave was removed from the aluminum block and cooled to room temperature in a water bath. The remaining gases were discharged and the vials containing reaction products were removed from the autoclave. The reaction mixture was filtered through a Celite pad (~3 cm), washed with ethyl acetate (3 x 20 mL) and methanol (2 x 20 mL). The solution was concentrated desired product 1s a yellow oil (975 mg, 85%).

3. GC analysis of the gas phase

GC Conversion and yields were determined by GC-FID, HP6890 with FID detector, column HP530 m x 250 mm x 0.25 µm. Analysis of the gas sample in the dehydrogenation process was performed using GC HP Plot Q (FID – hydrocarbons, Carboxen / TCD - permanent gases), Ar - carrier gas. The GC was externally calibrated using certified gas mixtures from commercial suppliers (Linde and Air Liquide) with the following gas vol%:

- H$_2$: 1%, 10%, 25%, 50%, 100%
- CO: 10 ppm, 100 ppm, 250 ppm, 1000 ppm, 1%, 10%
- CO$_2$: 1%, 50%
- CH$_4$: 1%

The systems allow for the determination of H$_2$, CH$_4$, CO and CO$_2$ within the ranges:

- H$_2$ ≥ 0.5 vol% - 100 vol%
CO ≥ 10 ppm
CO₂ ≥ 100 ppm - 100 vol%
CH₄ ≥ 1 ppm

Fig. S1. Gas composition analysis by GC of the gas mixture after 48h in the absence of nitroarene substrate (H₂:CO:CO₂ – 1.55: 98.36: 0.088).

Fig. S2. Gas composition analysis by GC of the gas mixture after 24h in the presence nitrobenzene. (H₂:CO:CO₂ – 1.31: 93.83: 4.83).
4. Deuterium labeling experiments NMR spectra

Fig. S3. Deuterium labeling experiments
5 Hot filtration tests

A set of reactions was set according to the general hydrogenation procedure described above. Hydrogenation of nitrobenzene was stopped at a certain time and the autoclave was cooled to room temperature and degassed. Vials containing reaction mixtures were heated to 50°C in an aluminum block under stirring. Then the reaction mixtures were quickly filtered through a preheated pipette, filled with celite (~1 cm). The filtrate was analyzed by GC (Yield A) and collected in a separate vial with a stirring bar. After the addition of 100µL of H₂O the vial was capped and transferred back into the autoclave for addition 16h under standard reaction conditions. The reaction mixture was again analyzed by GC (Yield, B).

<table>
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<tr>
<th>Entry</th>
<th>Time, h</th>
<th>TEA, equiv.</th>
<th>Yield, A, %</th>
<th>Yield B, %</th>
<th>Fe (ppm)</th>
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<td>33</td>
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</tr>
<tr>
<td>4</td>
<td>2</td>
<td>0</td>
<td>16</td>
<td>16</td>
<td>Not determined</td>
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</table>

Table S1. Summary of hot filtration tests

6. Photographs of the iron catalyst after recycling

![Fig. S4](image_url). Fresh Fe₃O₄/NGr@C catalyst (left); used Fe₃O₄/NGr@C catalyst (right).
7. NMR spectral charts
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Ryabchuk RP2-89-1
Au1H CDCl3 (C:\Bruker\TopSpin3.5\ff) 1804 21

\[
\begin{align*}
\text{NC} & \quad \text{NH}_2 \\
2n & \\
\end{align*}
\]

Ryabchuk RP2-89-1
Au13C CDCl3 (C:\Bruker\TopSpin3.5\ff) 1804 21

\[
\begin{align*}
\text{NC} & \quad \text{NH}_2 \\
2n & \\
\end{align*}
\]