

Supplementary Information

Efficient and highly selective iron-catalyzed reduction of nitroarenes to anilines

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1. Procedure for catalyst preparation (Fe-phenanthroline/C):

Appropriate amount of $\text{Fe}(\text{OAc})_2$ and 1,10-phenanthroline (Fe:Phenanthroline=1:2) in 75 mL ethanol was stirred for 20 minutes at room temperature. Then, vulcan XC72R carbon powder was added and the whole reaction mixture was refluxed at 60 °C for 3 hours. The reaction mixture was cooled to room temperature and ethanol was removed. The solid sample obtained was dried at 60 °C for 12 hours. The dried sample was grinded to a fine powder. Then, the grinded powder was pyrolyzed at 800 °C for 2 hours in argon atmosphere and cooled to room temperature.

Elemental analysis of Fe-Phenanthroline/C (Wt%): C = 89.59, H = 0.32, N = 1.16, Fe = 1.24, O = 7.69

Elemental analysis of Fe-Phenanthroline/C (Atom%): C = 92.72, N = 1.03, Fe = 0.28, O = 5.98

XPS data of Fe-Phenanthroline/C (Atom%): C = 90.26, N = 1.5, Fe = 0.3, O = 7.82

TEM Measurements

The TEM measurements were performed at 200kV on a JEM-ARM200F (JEOL) which is aberration corrected by a CESCOR (CEOS) for the STEM applications. The TEM measurements were performed at 200kV on a JEM-ARM200F (JEOL) which is aberration corrected by a CESCOR (CEOS) for the STEM applications. The microscope is equipped with a JED-2300 (JEOL) EDXS spectrometer for chemical analysis. The HAADF imaging was performed with spotsize 6c and a 40 μ m condenser aperture.

Preparation of the TEM sample: The sample was deposited on a holey carbon supported grid mesh 300 and transferred to the microscope.

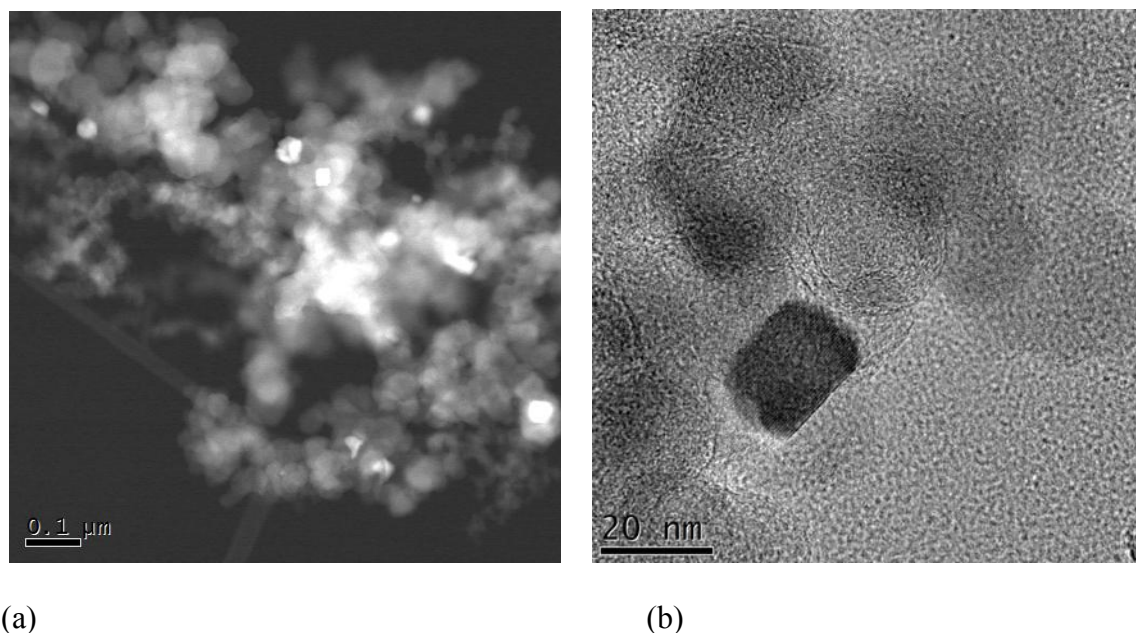


Figure S1-TEM images of Fe-phenanthroline/C (1.24 Wt% Fe)

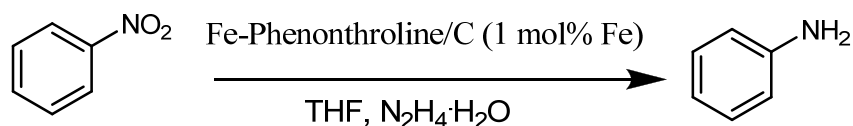
(a): STEM-HAADF: survey. (b): HRTEM image of a Fe-particle at the carbon support

2.General procedure for nitro arene reduction

The corresponding nitro compound (0.5 mmol) was dissolved in 5 mL THF in a pressure tube. Then, hydrazine hydrate (2 mmol), Fe-phenanthroline/C (1 mol% Fe) and hexadecane (100 μ L) as internal standard were added. The reaction mixture was stirred for 10 hours at 100 $^{\circ}$ C. After cooling the reaction mixture to room temperature, the catalyst was filtered off, and the sample of the mixture was directly subjected to GC analysis. Conversion and yields were determined by GC-FID (HP6890 with FID detector, column HP530 m x 250 mm x 0.25 μ m) and compared with authentic samples. Quantitative and qualitative analysis of all amines were made by GC, GC-MS and

identified by comparison with authentic samples. The reaction was scaled up by a factor of 10 for three substrates. The corresponding amines were isolated and purified by column chromatography.

3. Table S1 . Testing of different parameters and optimizing the reaction conditions in presence of Fe-phenanthroline/C ^[a]



Entry	Time [h]	Temperature [°C]	N ₂ H ₄ ·H ₂ O [mmol]	Conv. [%]	Yield [%]
1	15	100	2.0	100	99
2	15	100	1.5	75	72
3	15	100	1.0	60	59
4	15	100	3.0	100	99
5	15	80	2.0	60	48
6	15	60	2.0	51	42
7	15	RT	2.0	41	11
8	10	100	2.0	100	99
9	8	100	2.0	99	97
10	6	100	2.0	97	96

[a] Reaction conditions: 0.5 mmol nitrobenzene, Fe-Phenanthroline/C (1 mol%Fe).

4. Selectivity and intermediates in the nitrobenzene reduction

Regarding the mechanism, we believe that this iron-catalyzed reduction sequence follows the accepted reduction for nitroarenes.²⁴ Hence, in general nitrosobenzenes, azoxybenzenes, azobenzenes, and hydrazobenzenes can be expected as intermediates. Some of these intermediates constitute potential safety hazards, which should not be accumulated during the reaction. Investigating the kinetics of the reaction of nitrobenzene in the presence of Fe-phenanthroline/C under optimized conditions showed very high selectivity (>97%-99%) for aniline throughout the reaction (Figure 1). We have not detected any other intermediates in the reaction mixtures. These results also explain the high selectivity for the chemoselective reduction of 1,4-dinitrobenzene.

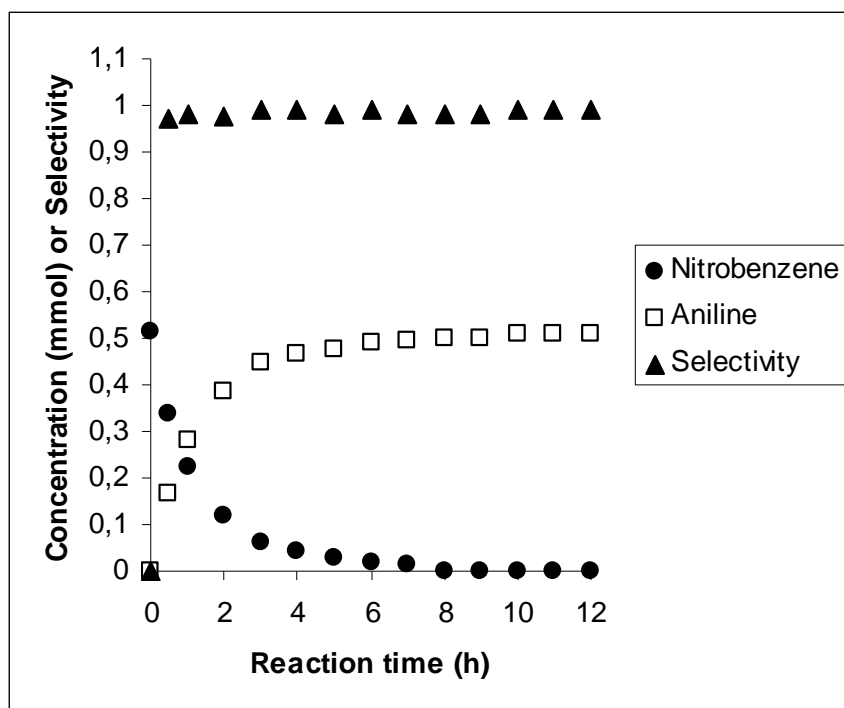


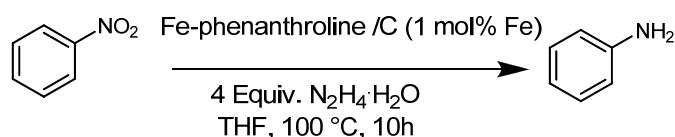
Figure 1: Reduction of nitrobenzene: Concentration of reactants, product, and selectivity at different reaction times

Reference

- 24 a) F. Haber, *Z. Elektrochem. Angew. Phys. Chem.* **1898**, 22, 506; b) R. M. Dyson, M. Hazenkamp, K. Kaufmann, M. Maeder, M. Studer, A. Zilian, *J. Chemometrics* **2000**, 14, 737.

5. Recycling of catalyst (Fe-phenanthroline/C).

The recycling of the catalyst system was carried out for the reduction of nitrobenzene. In each run, after the reaction, the catalyst was separated by centrifugation, washed thoroughly with ethyl acetate and dried for 15 hours under high vacuum. Then, the dried catalyst was used further, without any purification.



Run	1	2	3	4	5	6	7	8
Yield	99	98	98	99	97	99	97	93