Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Bulk Iron Pyrite as a Catalyst for the Selective Hydrogenation of Nitroarenes

James R. Morse, Juan F. Callejas, Albert J. Darling and Raymond E. Schaak*

Department of Chemistry and Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802, United States.

E-mail: res20@psu.edu

Contents:

1. General Methods

Chemicals. Iron pyrite (FeS_2) was purchased from both STREM (95%) and Alfa Aesar (naturally occurring mineral grains 1.5-4.8 mm), and both were found to be equally active and selective catalysts for nitroarene hydrogenation. 1-bromo-4-nitrobenzene (99%), 1-chloro-4-nitrobenzene (99%), 1-iodo-4-nitrobenzene (98%), 1-ethynyl-4-nitrobenzene (97%), 3-nitrostyrene (96%), 4-nitrobenzamide (98%), 4-nitrobenzonitrile (97%), 4’-fluoro-3’-nitroacetophenone (97%), 4-nitrobenzenesulfonamide (97%), aniline (>99%), 4-chloroaniline (98%), 4-ethynylanilne (97%), 3-vinylaniline (97%), 4-iodoaniline (98%), 4-aminobenzamide (98%), 4-aminobenzonitrile (98%), 4-aminobenzoic acid (99%), methyl-4-aminobenzoate (98%), nirosobenzene (97%), N-phenylhydroxylamine (97%), tetrahydrofuran [THF, 250 PPM BHT inhibitor (>99%)] and tetradecane (99%) were purchased from Sigma-Aldrich. 4-nitrobenzaldehyde (99%), 4-bromoaniline (99%) and methyl-4-nitrobenzoate (98%) were purchased from TCI America. Nitrobenzene (99%) was purchased from Acros Organics. 4-nitrobenzoic acid (99%) was purchased from Alfa Aesar. 4-aminobenzaldehyde (98%) was purchased from AK Scientific. 10% Pt on activated carbon powder was purchased from Premetek. All chemicals were used as received without further purification.

Hydrogenation Reactions. Iron pyrite was first pulverized by grinding with a mortar and pestle for 5 minutes. In a typical reaction, 50 mg of freshly ground iron pyrite was added to a septum capped glass vial along with a Teflon coated magnetic stir bar, 4 mL THF, 0.5 mL deionized water, and 0.5 mmol substrate. (For the substrates 4-nitrobenzamide, 4-nitrobenzenesulfonamide, and 4’-fluoro-3’-nitroacetophenone, a 1:1 ratio of deionized water to THF of equivalent volume was used to facilitate substrate dissolution.) A 300-mL Parr stainless steel autoclave (4766-T- SS-3000- VGR) was used for all hydrogenation reactions. The septum cap of every sample was punctured with a disposable 18 gauge needle, to allow the partitioning of H_2 into the vial. Once prepared and sealed, the autoclave was flushed twice with H_2 gas at 25 bar in order to remove ambient air and then filled to its final pressure of 50 bar H_2 gas. Once pressurized, the autoclave was heated to 120 °C and held at that temperature for 18 h, unless otherwise noted. The reaction was cooled to room temperature, the H_2 atmosphere was discharged, and the samples were prepared for GC-MS as described below. When 5 mg of freshly ground iron pyrite was used to hydrogenate 3-nitrostyrene under otherwise identical conditions, only ~ 20% conversion was achieved, indicating that optimal catalyst loadings are needed.

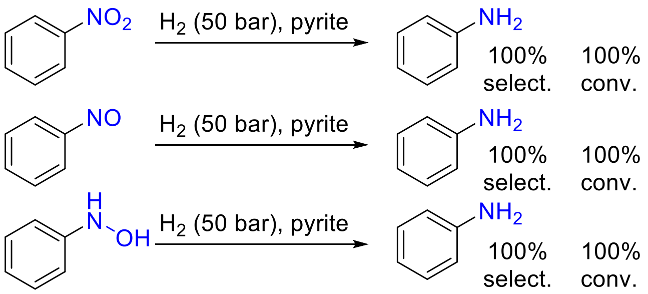
Surface Area Analysis. Nitrogen adsorption analysis was performed at 77K, using an Accelerated Surface Area and Porosimetry Analyzer (ASAP 2420; Micrometritics Instrument Corp.). Surface area was calculated using the Brunauer, Emmett and Teller (BET) equation [S. Brunauer, P. H. Emmet, E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309-319]. Prior to the measurement, the sample was degassed at 373.15 K for 240 min under 4 μm Hg vacuum. Measurements were acquired using the commercial STREM pyrite sample both before and after the material was ground to a powder using a mortar and pestle. The BET surface area of this material was 1.8 m^3 g^{-1} for each sample.

Recycling Experiments. Six individual iron pyrite samples were tested under identical conditions for recyclability (5 successive cycles each) to generate the data and error bars included in Fig. 2. For each of the six experiments, 50 mg of bulk pyrite was ground and reacted with 0.5 mmol of 3-nitrostrene at 50 bar H_2 and 120 °C for 18 hours, as described above. Once the reaction was completed, the septum capped vial containing the sample was sonicated for ~30 s to agitate and suspend the particulates in the sample vial. This suspension was centrifuged at 4000 RPM for 5 min to collect the solid pyrite. The supernatant was then decanted and prepared for GC-MS analysis, as described below. 5 mL of ethanol was added to the centrifuged pyrite (which formed a pellet at the bottom of the centrifuge tube), and then sonicated for an additional 30 s. This suspension was centrifuged again at 4000 RPM for 5 min. The ethanol supernatant was decanted, and this washing procedure was performed one more time. After these washing steps, the pyrite pellet was suspended in 4 mL THF using sonication. This iron pyrite suspension was transferred to the original 20-mL septum-capped vial, along with 0.5 mL of deionized water and 0.5 mmol of 3-nitrostyrene. The sample was then hydrogenated under identical reaction conditions. This procedure was followed until five total reactions were carried out on the same pyrite catalyst. After five runs, the pyrite sample was dried overnight, under vacuum, before subsequent characterization.

GC-MS Analysis. After hydrogenation, tetradecane was added to the samples as an internal standard. The samples were then diluted with THF, and centrifuged at 4000 RPM for five minutes to remove any suspended pyrite. The products were characterized by GC-MS and quantified using calibration curves generated from commercial reagents. When no substrate signal was observed, the reaction was assumed to go to 100% conversion. Similarly, when only the product peak was observed, 100% selectivity was assumed.

Catalyst Characterization. Powder X-ray diffraction (XRD) patterns were collected with a Bruker Advance D8 X-ray diffractometer and Cu Kα radiation at room temperature. Simulated powder XRD patterns were produced using the CrystalMaker and CrystalDiffract software suite. Scanning electron microscopy (SEM) imaging was performed using a Nova NanoSEM 630 FESEM (FEI) at an accelerating voltage of 20 keV. X-ray photoelectron spectroscopy (XPS) experiments were performed using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al Kα X-ray source (hν = 1,486.7 eV) and a concentric hemispherical analyzer. Charge neutralization was performed using both low energy electrons (<5 eV) and argon ions. The binding energy axis was calibrated using sputter cleaned Cu foil (Cu $2p_{3/2}$ = 932.7 eV, Cu $2p_{3/2}$ = 75.1 eV). Peaks were charge referenced to the CH_x band in the carbon 1s spectra at 284.8 eV. Measurements were made at a takeoff angle of 45° with respect to the sample surface plane. This resulted in a typical sampling depth of 3-6 nm (95% of the signal originated from this depth or shallower). Quantification was done using instrumental relative sensitivity factors (RSFs) that account for the X-ray cross section and inelastic mean free path of the electrons.

2. Supplementary Data



[1] All reactions were run under 50 bar H_2 at 120 $^{\circ}$C for 18 h.

Fig. S1. Conversion of nitrobenzene, nitrosobenzene, and n-phenylhydroxyl amine to aniline using pyrite under standard reaction conditions.

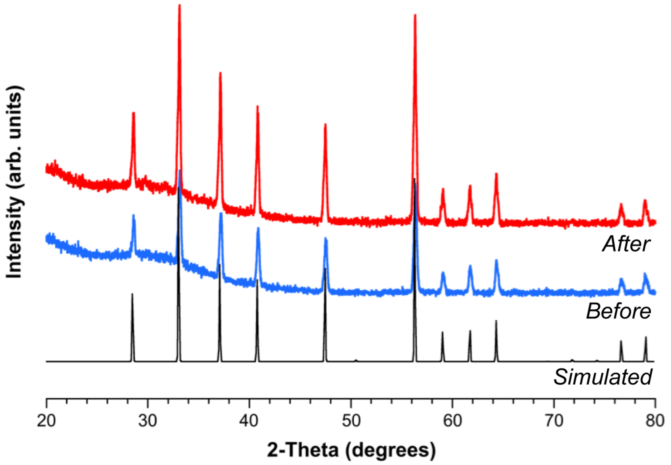


Fig. S2. Powder X-ray diffraction (XRD) patterns for the ground pyrite catalyst before (blue) and after five hydrogenation cycles of 3-nitrostyrene (red). The simulated pyrite XRD pattern is shown in black below the experimental patterns.

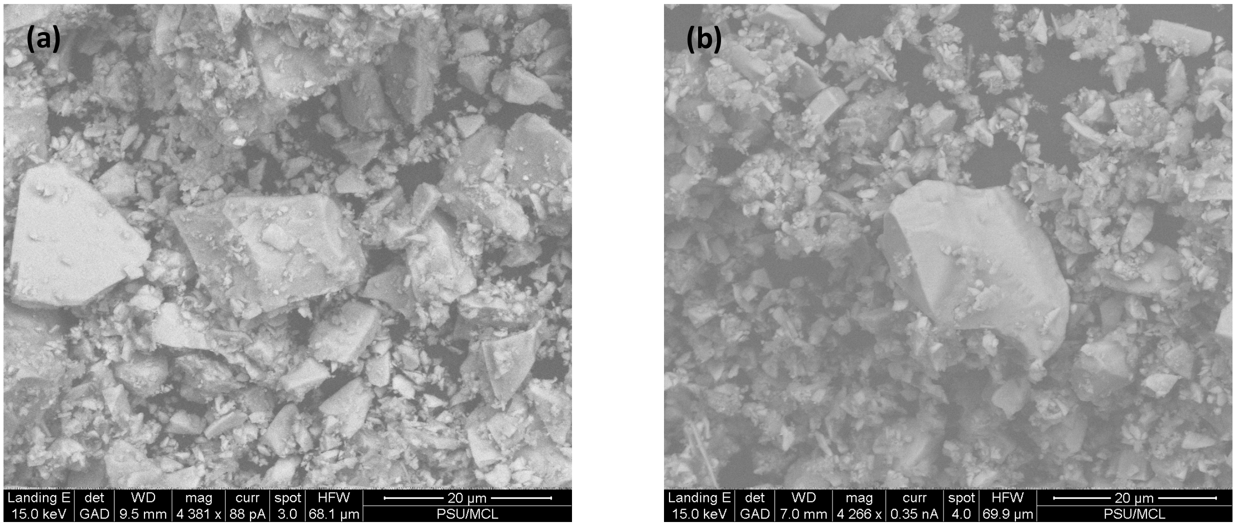


Fig. S3. SEM images of the pyrite sample (a) before and (b) after five hydrogenation cycles of 3-nitrostyrene.

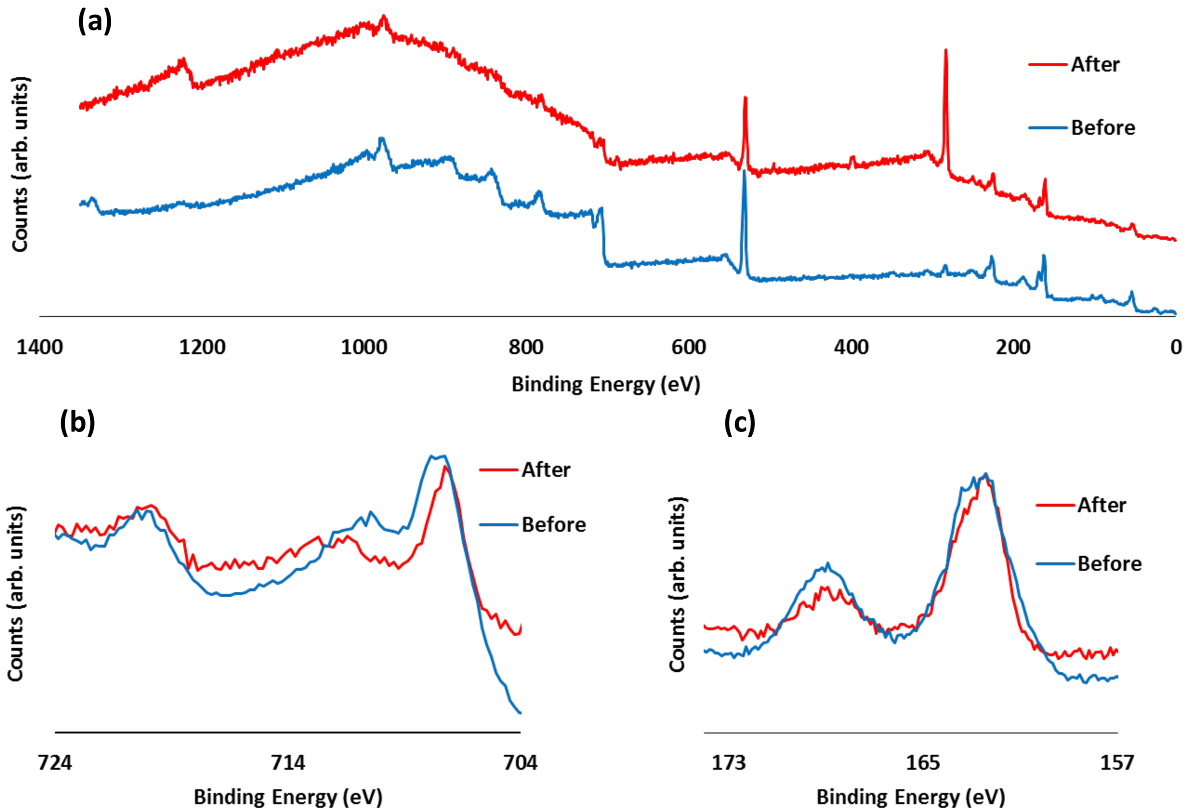


Fig. S4. (a) XPS spectra for the pyrite sample before (blue) and after (red) five hydrogenation cycles of 3-nitrostyrene. **(b)** High resolution scans of the Fe $2p_{3/2}$ region for each sample. **(c)** High resolution scans of the S $2p_{3/2}$ region for each sample.