

Pyrite nanoparticles: an earth-abundant mineral catalyst for activation of molecular hydrogen and hydrogenation of nitroaromatics

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Experimental Section

Preparation of FeS₂ nanoparticles: 0.994 g of ferrous chloride (FeCl₂·4H₂O) and 0.960 g of sulfur powder were dispersed into 40 mL of absolute ethanol and 20 mL of oleylamine under sonication. The suspension was magnetically stirred for 0.5 h, and then transferred into a 100 mL stainless steel autoclave. The suspension was maintained at 220 °C for 10 h, and then cooled to room temperature naturally. The precipitate was filtered off, washed with acetone, absolute ethanol and distilled water, and dried in a vacuum environment at 40 °C for 12 h.

Chemical titration: 0.10 g of FeS₂ was dispersed in 5 ml deionized water, then sufficient amount of hydrochloric acid was added in order to completely dissolve FeS₂. The obtained solution was diluted to 100 ml, applied as sample solution. Subsequently, 25.00 ml sample solution was transferred to 250 ml conical flask, and 30 ml deionized water and 15 ml 3 mol/L H₂SO₄ solution were added to get A solution. In next, 0.01 mol/L KMnO₄ solution was added into A solution until the solution exhibited reddish. The content of Fe can be calculated by the formula (1):

$$\omega_{\text{Fe}} = \frac{5C_{\text{KMnO}_4} V_{\text{KMnO}_4} M_{\text{FeS}_2}}{1000 \times m_s \times \frac{25.00}{100.00}} \quad (1)$$

which ω_{Fe} is the content of Fe; V_{KMnO_4} is the consumption of KMnO₄ solution; C_{KMnO_4} is Concentration of KMnO₄ solution; M_{FeS_2} is weight of FeS₂ and m_s is the molar mass of FeS₂.

The content of Fe is 45.71% by chemical titration, which is close to the standard value (46.55%) in FeS₂.

Hydrogenation of nitroaromatics: The hydrogenation of nitroaromatics was conducted in a sealed stainless autoclave with magnetical stirring. 1.0 mmol of nitroaromatics and 80 mg of FeS₂ catalyst were dispersed in 10 ml of isopropanol, and the suspension was then sealed in the autoclave. All reactions were reacted under 0.5 MPa of H₂ and 60 °C for 7 hours unless otherwise specified. The reaction products were analysed by Gas chromatography mass spectroscopy (GC-MS, Bruker SCION SQ 456 GC-MS system, Karlsruhe, Germany).

H₂-TPD experiments: In the H₂-TPD experiments, 100 mg of the FeS₂ sample was pretreated in Ar flow (25 ml/min) at 573.15 K for 2 h. After the pretreatment, the temperature was naturally decreased to 313.15 K and H₂ was inducted to expose the FeS₂ sample for 10 min. Next the sample was purged by Ar flow to remove unabsorbed H₂ until the monitor signal did not change. At last, the TPD spectra were recorded in the temperature range from 313.15 K to 900 K for different heating rates (8 K/min, 10 K/min, 12 K/min, 14 K/min).

Computational Details

Our calculations were based on the density functional theory as implemented in the Vienna Ab Initio

Simulation Package (VASP).¹ The electronic structure is described within the spin-polarized density functional framework employing the PW91 functional method.² A plane-wave basis set in conjunction with the PAW method³ has been used with a cutoff of 400 eV. For the adsorption states, we employ a 2×2 orthorhombic surface supercell with $a = b = 10.830 \text{ \AA}$ and $c = 21.661 \text{ \AA}$. The pyrite slab was nine atomic layers thick, and an about 15 \AA vacuum layer separates it from its periodic images in direction c . The bottom three layers have been kept fixed during the calculations. Dipole corrections accessible in VASP have been included for all systems. We have used a $3 \times 3 \times 1$ Monkhorst-Pack k-point set to sample the Brillouin zone which has been shown to be sufficient to obtain structural and energetic properties within the aspired accuracy (0.001 \AA and 0.02 eV/\AA^2).

The adsorption energy is calculated according to $E_{\text{ads}} = E_{\text{X/slab}} - [E_{\text{slab}} + E_{\text{X}}]$, where $E_{\text{X/slab}}$ is the total energy of the slab with adsorbates in its equilibrium geometry, E_{slab} is the total energy of the bare slab, and E_{X} is the total energy of the free adsorbates in gas phase, which is calculated in a $(10 \times 10 \times 10)$ cell. When a nitrobenzene adsorbs on the surface of FeS_2 , the adsorption energy is -2.29 eV .

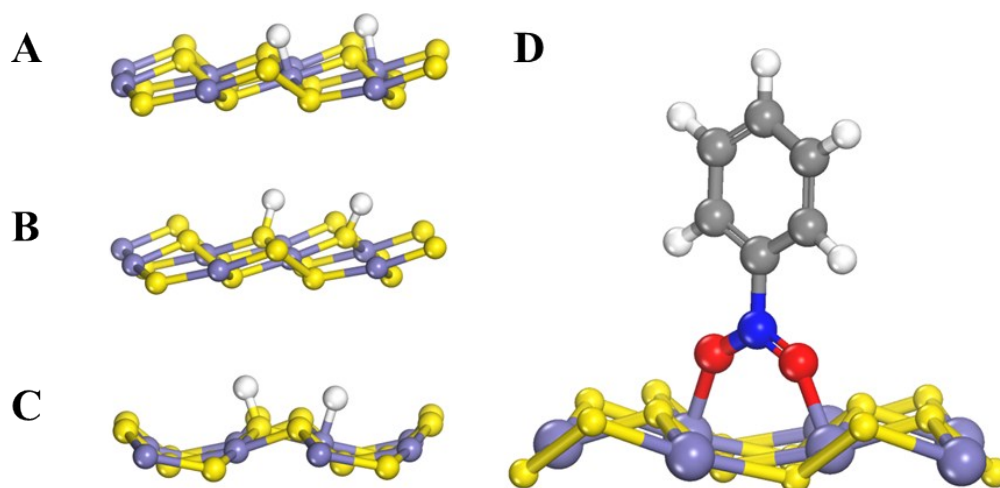


Figure S1. Adsorption of hydrogen and nitrobenzene on $\text{FeS}_2(100)$. (Fe/ purple, S/yellow, C/gray, N/blue, O/red, H/white).

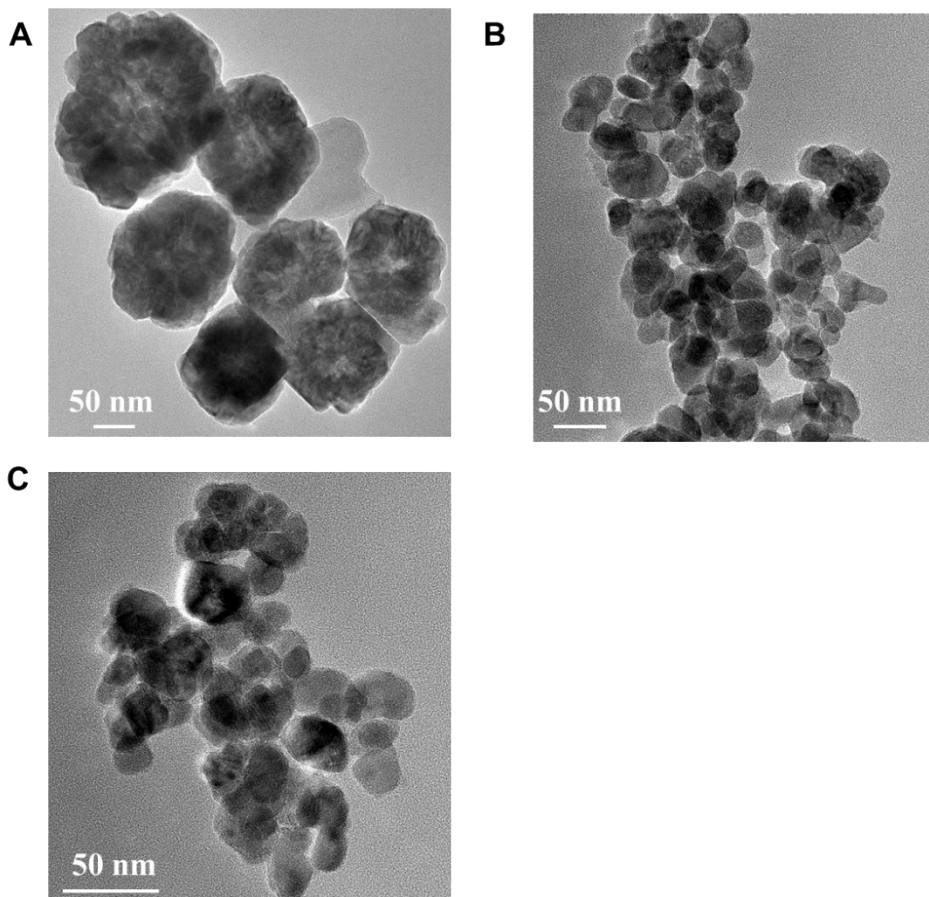


Figure S2. TEM images of the FeS₂ nanoparticles with different sizes (The size of A, B, C are 200-300nm, 50-100 and 30-50nm, respectively).

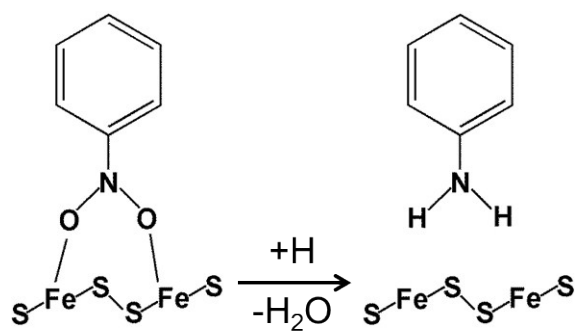


Figure S3. Proposed mechanism for the catalytic hydrogenation of nitrobenzene on FeS₂ surface.

Table S1. Size distributions and surface area of FeS₂ particles prepared under different conditions.

Entry	FeCl ₂ ·4H ₂ O/g	S/g	Size/nm
1	0.398	0.385	200~300
2	0.596	0.577	50~100
3	0.795	0.767	30~50
4	0.994	0.960	8

Table S2. Hydrogenation of nitrobenzene to aniline on various catalysts.

Entry	Catalyst	t/h	R/mmol·h ⁻¹ ·g ⁻¹	Conv. (%)	Select. (%)	Ref.
1	Ni-5/SiO ₂ -AC ^a	4.0	6.77	19.6	56.5	[4]
2	Ni-5/SiO ₂ -Ni ^a	4.0	7.14	20.1	58.1	[4]
3	C ₆₀ ^b	4.0	5.58	21.4	46.4	[5]
4	C ^c	24.0	0.33	99.0	80.0	[6]
5	FeS ₂ ^d	6.5	5.02	52.2	99.0	Our work

^a Reaction condition: 0.200 g of catalyst, 0.0489 mol nitrobenzene, 30 mL of ethanol solvent at 90 °C, 1.0 MPa of H₂. ^b Reaction condition: 0.036g of catalyst, 0.0081 mol nitrobenzene, 40 mL of tetrahydrofuran solvent at 140 °C, 2.0 MPa of H₂. ^c Reaction condition: 0.0010 mol nitrobenzene, 0.100 g catalyst, 3 mmol KOH, 2 ml isopropanol, argon atmosphere at 100 °C. ^d Reaction condition: 0.080 g of catalyst, 0.0050 mol nitrobenzene, 10 mL of isopropanol at 90 °C, 1.0 MPa of H₂. Note: Here we employed

Notes and references

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