Supplementary Material

Bifunctional Fe₂O₃ catalyst for hydrogenation and transfer

hydrogenation of nitroarenes

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Experimental Materials

All reaction reagents were of analytical grade and used as purchased without further purification, purchased from Macklin Biochemical Co., Ltd. Deionized water was used throughout the experiments.

Characterization

Gas chromatography (GC) (Shimadzu GC-2014 ATFSPL, FID, SH-RTX-5 capillary column) and gas chromatography-mass spectrometry (GC–MS) (Agilent 5977E, HP-5 capillary column) are applied to determine the reaction conversion and selectivity using n-hexadecane as the internal standard. Mechanism experiment was analyzed by high performance liquid chromatography (HPLC). The mobile phase consisted of methanol and water, the volumetric ratio of which was kept at 9:1 and a Luna 5 μ m C18 4.6 mm × 250 mm column (Shimadzu) was used. To identify reaction products, DAD detector was set at 230nm wavelengths, N-phenylhydroxylamine (PHA), aniline (AN), nitrobenzene (NB), nitrosobenzene (NSB), azobenzene (AB) and azoxybenzene (AOB) were detected in turn.

The crystallographic structure of the solid samples was investigated at room temperature using powder X-ray diffraction (XRD, Rigaku D/max-2400 diffractometer, Cu-Kα radiation,) at a scanning rate of 3°·min⁻¹. Raman spectra were recorded on an in Via Renishaw confocal microscope with 633 nm laser excitation. Chemical bonding information of the samples was acquired with Fourier transform infrared spectroscopy (FT-IR, Nicolet NEXUS 670) using the potassium bromide (KBr) pellet technique. To make the KBr pellets, about 1 mg of sample was diluted with 100 mg of KBr powders. Each FT-IR spectrum was collected after 32 scans with a resolution of 4 cm⁻¹ from 400 to 4000 cm⁻¹. Scanning electron microscopy (SEM, Apreo S) and transmission electron microscopy (FEI Talos F200s) could observe the structure of catalysts. The Brunauer-Emmett-Teller (BET) analysis could obtain the specific surface area, pore volume and pore width using a Micromeritics ASAP 2020 instrument. Temperature-programmed desorption (TPD) experiments were performed on the ChemiSorb 2720 Pulse

Chemisorption System produced by Micromeritics, USA with a TCD (thermal conductivity detector). In a typical NH₃-TPD process, the sample (50 mg) was pretreated under an Argon flow (25 mL·min⁻¹) at 373K for 30 min. After cooling to 353K, the sample was exposed to repeated 10% NH₃/Argon pluses for 30 min. Subsequently, the sample was purged at 303K with Argon to remove the physical adsorbed NH₃ species, and then the temperature was brought up to 1073k at a ramping rate of 10 K·min⁻¹. The final TPD profile was obtained by applying subtraction treatment between the adsorbed curve (NH₃ species) with blank curve without adsorbing any probe molecular.

Catalyst Preparation

In a typical procedure, an aqueous solution composed of 10 mmol Fe(NO₃)₃·9H₂O in 100 mL H₂O was stirred at room temperature to get a homogenous solution. Then an ammonia solution was added drop wise to the mixed solution until Fe³⁺ were completely precipitated. After stirring for another 24 h, the slurry was filtered and washed by deionized water until free from anion impurities. Then a solid was obtained after drying at 60 °C overnight. The obtained solid was then calcined at different temperature, and amorphous Fe₂O₃ was completely synthesized.

Hydrogenation Procedure

The general procedure for the transfer hydrogenation of nitrobenzene to aniline was as follows: 1 mmol nitrobenzene (NB), 1.5 mmol N_2H_4 · H_2O , 50 mg catalyst and 2 mL EtOH were added to a round bottom tube under air with magnetic stirring at room temperature for 2 hours. When using H_2 as reduce agent, 1 mmol NB, 50 mg Catalysts and 10 mL solvent were added into the stainless-steel autoclave reactor, and H_2 was purge the reactor 5-6 times to remove the air, then fill it to a specified pressure.

Acid Titration Method

Prepare a standard aqueous solution containing a certain amount of N_2H_4 · H_2O . Accurately transfer 100 mL of the solution using a pipette, and then mix it separately with 10, 20, 30, 50, and 100 mg samples. Stir the mixture magnetically for 30 minutes to ensure thorough adsorption of hydrazine hydrate on the surface of the samples. Then, filter the solution. The filtrate contains hydrazine hydrate that has not been adsorbed by the catalyst samples. The amount of remaining hydrazine hydrate is determined by measuring the pH of the filtrate, indicating the catalyst's ability to adsorb hydrazine hydrate. In other words, the stronger the catalyst's ability to adsorb hydrazine hydrate, the less hydrazine hydrate remains in the filtrate, resulting in a lower pH value of the solution.

Substrate Adsorbing FT-IR and XPS Experiment

Substrate adsorbing FT-IR experiment: In a typical procedure, 1 mg of the catalyst and 10 μ L of N₂H₄·H₂O are mixed in an agate mortar. The mixture is ground thoroughly to ensure sufficient contact between the catalyst and substrate. Then, 100 mg of KBr powder is added to the mixture and ground again to achieve a homogeneous paste. The prepared sample is then pressed into thin sheets for FT-IR testing. For studying the interaction among N₂H₄·H₂O, nitrobenzene, and the catalyst, an additional 10 μ L of nitrobenzene is added to the mixture before repeating the same process.

Substrate adsorbing XPS experiment: The catalyst prepared under conditions same as the reaction conditions, sample II: Fe₂O₃-200, 1.5 mmol N₂H₄·H₂O and 2mL EtOH, magnetic stirred for 2 h, the mixture was filtered and dried at 60 °C; sample III: 50 mg Fe₂O₃-200, 1.5 mmol N₂H₄·H₂O, 1mmol NB and 2mL EtOH, and the following steps are the same as sample II.

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Entry	Catalysts (mg)	Solvent	AN Yield [%]
1	Fe ₂ O ₃ -200 (50)	MeOH	68
2	Fe ₂ O ₃ -200 (50)	EtOAc	28
3	Fe ₂ O ₃ -200 (50)	Toluene	40
4	Fe ₂ O ₃ -200 (50)	H_2O	23
5	Fe ₂ O ₃ -200 (50)	CH_2Cl_2	15
6	Fe ₂ O ₃ -200 (30)	EtOH	58
7	Fe ₂ O ₃ -200 (40)	EtOH	77
8	CeO ₂ -200 (50)	EtOH	1
9	Cr ₂ O ₃ -200 (50)	EtOH	1
10	NiO-200 (50)	EtOH	3
11	Mn ₈ O ₅ -200 (50)	EtOH	1
12	La ₂ O ₃ -200 (50)	EtOH	2
13	CoO-200 (50)	EtOH	3
14	ZrO ₂ -200 (50)	EtOH	1

Table S1 Catalytic performances under different conditions. ^a

^a Conditions: 1mmol NB, 1.5 mmol N₂H₄·H₂O, 2mL solvent, 2 h, room temperature, 800 rpm. Determined by GC using n-hexadecane as the internal standard.

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Catalyst	Т	Time	N_2H_4 · H_2O :	AN Yield	Ref.
	[°C]	[h]	NB	[%]	
Fe ₂ O ₃ -200	r.t.	2	1.5	99	This work
BNC	40	4	4	99	1
ISAS Co/NBPC	35	2	30	99	2
FeC700	100	1	4	83	3
NCS-800	50	1	2	69	4
Co@HCS-800	r.t.	0.1	30	99	5
CuFeS ₂	r.t.	4	8	99	6
Rh/Fe ₃ O ₄ /g-C ₃ N ₄ -N	110	0.1	3	99	7
Al/Ni-Pt/Ti	40	1	6	99	8
C ₆₀ -EDAC	100	4	60	92	9
NC-950	90	1	4	99	10

Table S2 Hydrogenation of nitrobenzene over different catalysts.



Figure S1. XRD patterns of the as-prepared catalysts.



Figure S2. SEM images of a) Fe_2O_3 -60, b) Fe_2O_3 -200 and c) Fe_2O_3 -300.



Figure S3. N_2 adsorption-desorption profiles.

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Entry	Catalysts	Surface Area [m ² ·g ⁻¹]	Pore Volume [cm ³ ·g ⁻¹]	Pore Size [nm]
1	Fe ₂ O ₃ -60	323.45	0.20	2.46
2	Fe ₂ O ₃ -200	225.91	0.17	3.03
3	Fe ₂ O ₃ -300	96.90	0.21	8.70
4	Fe ₂ O ₃ -200-NaOH	156.29	0.63	16.15
5	Fe ₂ O ₃ -200-Na ₂ CO ₃	238.45	0.19	3.17
6	Fe ₂ O ₃ -200-KOH	195.75	0.27	5.56
7	Fe ₂ O ₃ -200-K ₂ CO ₃	2.59	0.0049	7.52

Table S3 The properties of the as-prepared catalysts.



Figure S4. Fe 2p XPS pattern of as-prepared samples.

Table S4 Catalytic performances under different conditions using H₂. ^a

Entry	Catalysts (mg)	Solvent	AN Yield
			[%]
1	Fe ₂ O ₃ -200 [30]	Toluene	68
2	Fe ₂ O ₃ -200 [40]	n-hexane	28
3	Fe ₂ O ₃ -200 [50]	isopropanol	40
4	Fe ₂ O ₃ -200 [60]	n-octane	23
5	Fe ₂ O ₃ -200 [50]	EtOH	15
6	Fe ₂ O ₃ -200 [50]	n-hexane : isopropanol = 1:1	58
7	Fe ₂ O ₃ -200 [50]	n-hexane : isopropanol = 1:1	77
8	Cr ₂ O ₃ -200 [50]	n-hexane : isopropanol = 1:1	1
9	NiO-200 [50]	n-hexane : isopropanol = 1:1	1
10	Mn ₈ O ₅ -200 [50]	n-hexane : isopropanol = 1:1	3
11	TiO ₂ -200 [50]	n-hexane : isopropanol = 1:1	1
12	CoO-200 [50]	n-hexane : isopropanol = 1:1	2
13	ZrO ₂ -200 [50]	n-hexane : isopropanol = 1:1	3

^a Conditions: 1 mmol NB, 100 mg Catalysts, 10 mL solvent, 150 °C, 1 MPa H₂, 16 h, 800 rpm. Determined by GC using n-hexadecane as the internal standard.



Figure S5. (a) Recycle test of Fe_2O_3 -200 for the transfer hydrogenation of nitrobenzene. Reaction conditions: 1 mmol Nitrobenzene, 1.5 mmol N_2H_4 · H_2O , 50 mg catalyst, 2 mL EtOH as solvent, 2 h with black line and 1 h with red line, determined by GC. (b) Hot filtration experiment of Fe_2O_3 -200 by continuing the reaction after filtration of the catalyst. Reaction conditions are the same as former.



Figure S6. Cycle test of Fe_2O_3 -200 for the hydrogenation of nitrobenzene with H₂. Reaction conditions: 1 mmol NB, 100 mg Catalysts, 5 mL n-hexane and 5 mL isopropanol as solvent, 150 °C, 1 MPa H₂, 16 h with black line and 8 h with red line, 800 rpm, determined by GC. (b) Hot filtration experiment of Fe_2O_3 -200 with H₂.

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