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Base-free Transfer Hydrogenation of Nitroarenes Catalyzed by Micro-mesoporous Iron Oxide

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Abstract:

An efficient and practical protocol for the transfer hydrogenation of nitroarenes is developed employing flower-shaped micro-mesoporous iron oxide (MMIO) with formic acid as the reducing agent and tris[(2-diphenyl-ethyl)phosphine] as ligand in the absence of additional base. The recyclable catalytic system

enables the reduction of nitro group in broad range of substrates and evinces high tolerance with sensitive functional groups to deliver useful amines.

Introduction

Anilines and its derivatives are widely used as important organic intermediates in the chemical industry for the production of pharmaceuticals, agrochemicals, polymers, and dyes.^[1] For the synthesis of functionalized anilines, various protocols have been reported including the reduction of nitroarenes,^[2] amination of aryl halides,^[3] reduction of azides,^[4] amination of alcohols^[5] and reduction of nitriles.^[6] To date, the most efficient and versatile strategy for synthesizing aromatic amines is the selective reduction of aromatic nitro compounds, involving both catalytic and non-catalytic methods.^[7] The traditional metal-catalyzed nitro reduction requires stoichiometric amount of the metal catalyst and thus produces a copious amount of undesirable waste.

On the other hand, catalytic hydrogenations are classified as environmentally benign processes and are compatible with industrial processes.^[8] The limiting factor, however, of this system is that it requires precious metal catalysts and typically molecular hydrogen. The selective reduction in presence of other functional groups is also a challenge. One way to approach the problem relies on the replacement of rare and expensive precious metal catalyst with cheaper, earth-abundant alternatives and also to avoid the use of hazardous molecular hydrogen, by the application of more safer and greener hydrogen donors (transfer hydrogenation). Thus, the catalytic hydrogen transfer serves as an attractive and safer alternative to catalytic hydrogenation, where handling of hydrogen gas in autoclaves is normally required.^[9]

Significant strides have been made in transfer hydrogenation reactions by designing new catalysts and the use of benign hydrogen donors, including formic acid, formate salts and alcohols.^[10]

Research efforts aimed towards the development of highly efficient and economical catalyst system for the transfer hydrogenation is a desirable goal from sustainable chemistry point of view.^[11] The use of earth-abundant iron-based catalysts is of special interest to limit the use of precious and toxic metals, as it is relatively benign, and inexpensive element;^[12] studies have been performed using different forms of iron for selective reduction of nitroarenes.^[13]

Bianchini and co-workers reported the transfer hydrogenation of α,β -unsaturated ketones using a trihydride iron complex using cyclopentanol or 2-propanol as hydrogen source.^[14] Recently, Beller and co-workers demonstrated the use of well-defined iron complexes as an effective homogeneous catalyst for the reduction of nitroarenes employing formic acid as the reducing agent^[15] wherein the catalytic performance of this catalyst is highly dependent on the metal-ligand combination. Similar transformations have been achieved employing formates as hydrogen donors, with other metal-based catalytic systems,^[16a,b] including a report on mesoporous iron oxide nanoparticle assemblies deployed for chemoselective catalytic reduction of nitroarenes.^[16c]

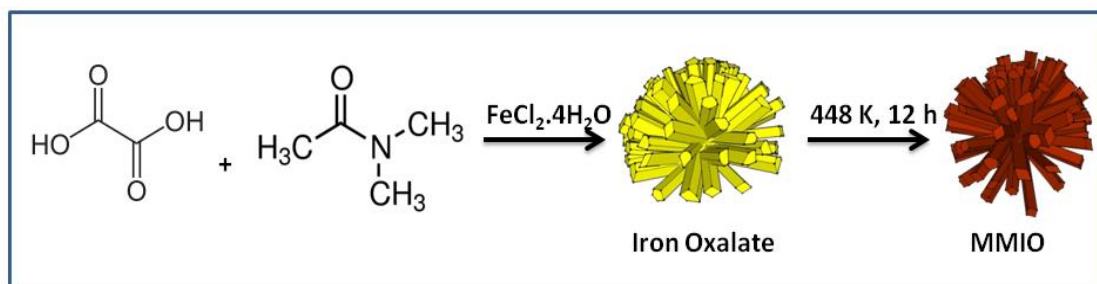
In our efforts to develop morphology-dependent catalytic protocols,^[17] recently we succeeded in a template-free solid-state synthesis of micro-mesoporous iron oxide (MMIO) catalyst via simple two-step synthetic procedure; ensuing 3D nanoassembly of hematite nanoparticles (5–7 nm) organized in a rod/flower-like morphology displayed excellent rate constant for the decomposition of H_2O_2 with greater efficiency for the degradation of organic pollutants.^[17]

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Scheme 1. Synthesis of iron oxide (MMIO) from iron oxalate.

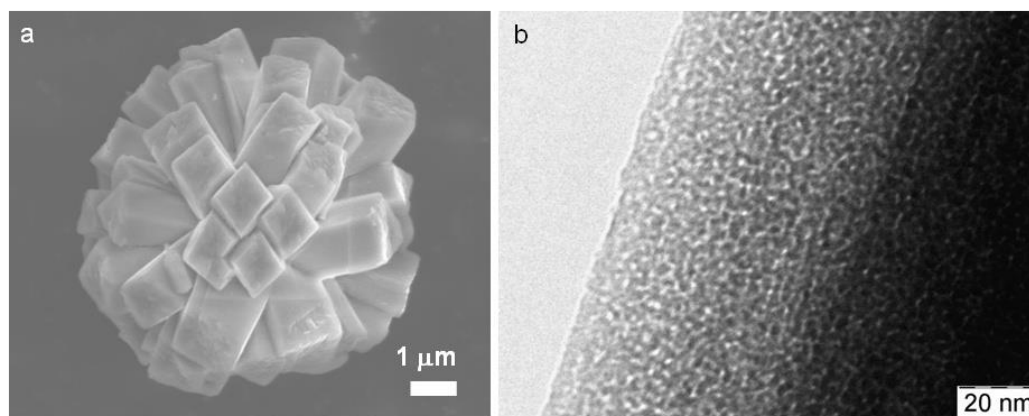


Figure 1. (a) FESEM image of MMIO catalyst and (b) HRTEM image showing nanosized hematite particles.

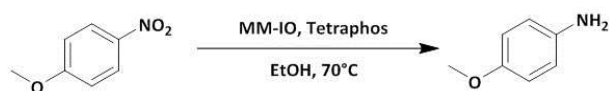
Results and Discussion

Herein, the first report that utilizes MMIO as a simple catalyst for the transfer hydrogenation of nitroarenes using biomass-derived formic acid as a reducing agent is described. Formic acid possesses several special attributes namely low toxicity, excellent stability, ease of transport, handling, and storage and its simple generation from hydrogen gas and carbon dioxide.^[18] Another advantage of formic acid over hydrogen gas is that the latter can lead to over reduction of aromatic substrates thus resulting in diminished chemoselectivity. The synthesis of MMIO catalyst is accomplished by the thermal treatment of iron oxalate precursors (Scheme 1).

The MMIO catalyst is well characterized by FESEM, HRTEM, XRD, N₂ adsorption desorption isotherm measurements and Mössbauer spectroscopy.^[17] The FESEM image of iron oxide is depicted in Figure 1a, which clearly shows intact flower shaped morphology. MMIO catalyst comprise several nanorods, and shows nanosized particles (5-7 nm) indicating the ultrafine building units of 3D nanocomposites (Figure 1 b). The lattice fringes of randomly oriented grains, which supports and indicates the crystalline nature of the MMIO catalyst. The sheets are clearly observed as crystalline and the lattice-fringes spacing matches with (110) atomic-planes distance of hematite (Figure S1).

The as-prepared MMIO, with ultra-small hematite nanoparticles collated into flower-like structure with high surface area (360 m²/g), exhibited good catalytic activity for the reduction of nitroarenes and is compatible with a wide variety of functional groups thus expressing the selectivity of the reaction. The combination of MMIO catalyst and the tetraphos ligand [tris[(2-diphenylphosphino)-ethyl]phosphine] led to significant catalytic activity for a wide range of substrates. To the best of our knowledge this is the first report for the reduction of nitroarenes using reusable MMIO catalyst without the aid of any support or a base.

As an initial stride, to develop an optimal catalytic system, various reaction parameters such as effect of temperature, different amount of iron oxide catalyst, solvent, ligand and the reaction time were studied by employing 4-methoxy nitrobenzene as benchmark substrate using ethanol as a solvent and formic acid as hydrogen source at 70 °C. Among the various phosphine ligands, tetraphos[tris[(2-diphenylphosphino)-ethyl]phosphine] exhibited good catalytic activity (Table 1, entries 1-6). To optimize the amount of ligand we used 3, 4, and 6 mol% resulting in 72%, 89% and 99% conversions respectively (Table 1, entries 6-8). Thus, 6 mol% became the optimized ligand concentration, the reaction time being fixed at 40 min (Table 1, entry 6). In the control experiment, no reaction (NR) occurred in the absence of ligand (Table 1, entry 9).

Table 1. Influence of the ligands.^a

Entry	Ligand	Conversion (%) ^b	Yield (%) ^b
1	Diphenylphosphine	<1	-
2	Triphenylphosphine	<1	-
3	Tricyclohexylphosphine	<2	-
4	Tri-n-butylphosphine	<3	-
5	Bis(2-diphenyl)phenylphosphinoethyl)phenylphosphine	<1	-
6	Tris[(2-diphenylphosphino)ethyl]phosphine(Tetraphos)	>99	95
7	Tris[(2-diphenylphosphino)ethyl]phosphine (Tetraphos)	>72	67
8	Tris[(2-diphenylphosphino)ethyl]phosphine(Tetraphos)	>89	84
9	None	-	-

^aReaction conditions: 4-nitroanisole (0.27 mmol), formic acid (2.7 mmol), catalyst (20 mg), ligands (6 mol%), ethanol (2 ml), 70 °C, 40 min.

^bDetermined by GC using n-hexadecane as internal standard. ^c3 mol%, ^d4 mol%.

Furthermore, we evaluated common iron-based catalysts such as FeCl₃, FeCl₂ and FeNO₃ for the reduction of 4-methoxy nitrobenzene but none of them worked (Table 2, entries 2-4). As compared to all other catalysts examined, only MMIO exhibited excellent conversion and yield (95%) while commercial iron (III) oxide afforded only 60% yield (Table 2, entries 5-6); no reaction occurred in the absence of catalyst (Table 2, entry 1). We believe that highly organized micro-mesoporous iron oxide with an encoded 3D organization is responsible for the excellent catalytic efficiency for the reduction of nitro compounds when compared to other iron sources such as commercial iron (III) oxide, and iron salts (Table 2). Additionally, the effect of temperature, time and loading of catalyst were studied and it was found that no reduction occurred at room temperature, while increasing the temperature to 50 °C led to 28% conversion (Table 2, entries 7 and 8).

Nevertheless, when the temperature was raised to 70 °C, 99% conversion was observed (Table 2, entry 6). However, below this temperature conversion was low even with longer reaction times. It was noticed that 40 min is sufficient time for this transformation (Table 2, entry 6) to achieve good yields, while shortened 30 min time gave 85% conversion (Table 2, entry 9). The optimum

amount of catalyst required for the completion of reaction was discerned by initially starting with 10 mg of catalyst and gradually increasing the amount up to 30 mg (Table 2, entry 10 and 11). It was observed that the yield increased with the amount of the catalyst and a maximum yield was obtained with 20 mg of the catalyst; both, the yield and the rate of the reaction remain unaffected by further increase in the amount of catalyst.

Table 2. Influence of the catalysts.^a

Entry	Catalyst	Conversion (%) ^b	Yield (%) ^b
1	-	-	-
2	FeCl ₂ ·4H ₂ O	<1	-
3	FeCl ₃ ·6H ₂ O	<1	-
4	FeNO ₃ ·9H ₂ O	<1	-
5	Commercial iron (III) Oxide	67	60
6	MMIO	>99	>95
7	MMIO	-	-
8	MMIO	28	-
9	MMIO	85	81
10	MMIO	72	68
11	MMIO	99	95

^aReaction conditions: 4-nitroanisole (0.27 mmol), formic acid (2.7 mmol), catalyst (0 mg), tetraphos (6 mol%), ethanol (2 ml), 70 °C, 40 min.

^bDetermined by GC using n-hexadecane as internal standard. ^cRT, ^d50 °C, ^e30 min, ^f10 mg catalyst, ^g30 mg catalyst.

Next, various solvents were investigated for the reduction of 4-methoxy nitrobenzene; changing the solvent dramatically affects the reaction efficiency. We observed highest yield in ethanol (Table 3, entry 1), whereas the yield was negligible in toluene, dimethylformamide (DMF), dichloromethane (DCM), water, acetonitrile and tetrahydrofuran (THF) (Table 3).

Table 3. Influence of the solvents.

Entry	Solvents	Conversion (%) ^b	Yield (%) ^b
1	EtOH	>99	95
2	Water	-	-
3	THF	-	-
4	Dioxane	3	-
5	Acetonitrile	-	-
6	Toluene	-	-
7	DCM	13	9
8	DMF	-	-
9	EtOH/H ₂ O (1:1)	<1	-

^aReaction conditions: 4-nitroanisole (0.27 mmol), formic acid (2.7 mmol), catalyst (20 mg), tetraphos (6 mol%), solvents (2 ml), 70 °C, 40 min. ^bDetermined by GC using n-hexadecane as internal standard.

The reducing agent was also examined (see Table 4) and to our satisfaction, the reaction with formic acid was very fast; complete reduction of nitrocompound occurred in 40 min at 70 °C with excellent conversion and yield compared to other reducing reagents (Table 4, entries 1-4).

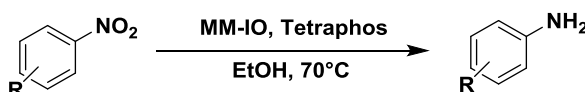
Table 4. Influence of the reducing agents^c

Entry	Reducing agent	Conversion (%) ^b	Yield (%) ^b
1	Formic acid	>99	95
2	Acetic acid	2	-
3	Ammonium formate	NR	NR
4	Hydrazine mono hydrate	77	71

^aReaction conditions: 4-nitroanisole (0.27 mmol), reducing agents (2.7 mmol), catalyst (20 mg), tetraphos (6 mol%), ethanol (2 ml), 70 °C, 40 min. ^bDetermined by GC using n-hexadecane as internal standard.

After the optimization of reaction parameters, we researched the scope and the limitations of this transfer hydrogenation protocol for a variety of functionalized nitroarenes using MMIO catalyst

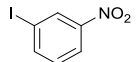
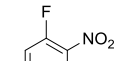
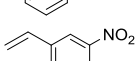
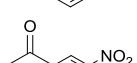
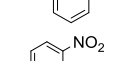
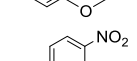
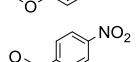
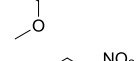
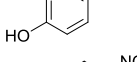
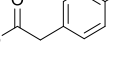
Table 5. MMIO catalyzed reduction of nitroarenes.^a



Entry	Substrate	Time	Conversion (%) ^b	Yield (%) ^b
1		40	>99	84
2		50	>99	83
3		60	>99	62
4		40	>99	85
5		40	>99	75
6		40	>99	87
7		40	>99	83

(Table 5). Numerous alkyl substituted aromatic nitroarenes were reduced to afford the corresponding anilines in good yields (Table 5, entries 2 and 4). The reduction of halogenated nitroarenes such as 4-chloro-, 3-bromo-, 4-fluoro-, and 3-iodo-nitrobenzenes was completed within 40 minutes in high yields (Table 5, entries 5-8), whereas 1-(*tert*-butyl)-4-nitrobenzene and 2-fluoronitrobenzene required little longer time (Table 5, entries 3 and 9). In the case of *m*-nitrostyrene, >99% conversion and 98% yield was observed (Table 5, entry 10). Importantly, various industrially significant nitroaromatic substrates containing other functional and reducible groups such as carbonyl, ether, methoxy, ester, and hydroxy were successfully reduced with good conversions and yields (Table 5, entries 11-16). Furthermore, the reduction of heterocyclic nitroarene was also performed; 5-aminoindole, an important intermediate in pharmaceutical industry, was obtained in good yield (Table 5, entry 17).

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8		40	>99	85
9		50	>99	80
10		40	>99	98
11		40	>99	82
12		40	>99	98
13		40	>99	95
14		40	>99	84
15		40	>99	85
16		40	>99	91
17		40	>99	85

^aReaction conditions - Nitroarene (0.27 mmol), HCOOH (2.7 mmol), catalyst (20 mg), tetraphos (6 mol%), ethanol (2 mL), 70 °C, 40 min.

^bDetermined by GC using n-hexadecane as internal standard.

The reduction of nitro compounds into amines has been recently described in the report of Papadas and co-workers,^[18] where they demonstrated that catalytic systems based on iron oxide nanoparticles (α -Fe₂O₃, Fe₃O₄ and β -Fe₂O₃) can effectively be used to promote hydrogen transfer reactions between a base (methylhydrazine) and the substrates. Our findings further support the existence of a similar scenario, in terms of efficiency and proclivity of iron based catalysts to act as hydrogen transfer activator/mediators, but highlights also that some differences in the catalytic pathway exist when reactions are carried out in acid environment. Here, the heterogeneous reaction employs formic acid as the source for the hydrogen transfer. The MMIO catalyst has high surface area and is characterized by large and positive zeta potential in water solution (+ 42mV). Therefore, the surface exposed Fe³⁺ cation are very prone to interact with negatively charged species, such as formate and PP₃ (triphenylphosphine) molecules in solution. These surface exposed Fe cations are characterized by a coordination sphere that is not fully filled by neighboring oxygen atoms as compared to those belonging to the intact (inner) α -Fe₂O₃ lattice. The envisioned catalytic path

followed by MMIO in acid environment is tentatively shown in Figure 2. In the first step, the surface exposed Fe cations readily interact with HCOO⁻/PP₃ in a way to reduce the excess of positive surface charges and form an intermediate configuration for the surface exposed iron (1), termed Fe[HCOO]PP₃ specie. The iron system progresses into Fe^{δ+}[H]PP₃ (2), upon decomposition of formic acid into CO₂, forming the catalytically active specie that is responsible for the transfer of electron and proton to the substrates, the nitro-compounds. The catalytic reduction of Ar-NO₂ to Ar-NH₂ in acid can evolve along two distinct pathways, as shown in scheme 2 along the sequence of reactions depicted by path (1) and (2). In the pathway (1), is assumed the occurrence of consecutive reduction steps of the nitroso compound through hydroxylamine and finally amine, while in pathway (2) the cross-reaction between the nitroso compound and a neighboring formed hydroxylamine molecule proceeds towards formation of a hydrazo intermediate that further evolves into amine. At the present stage, we cannot discriminate which is the dominant reduction pathway.

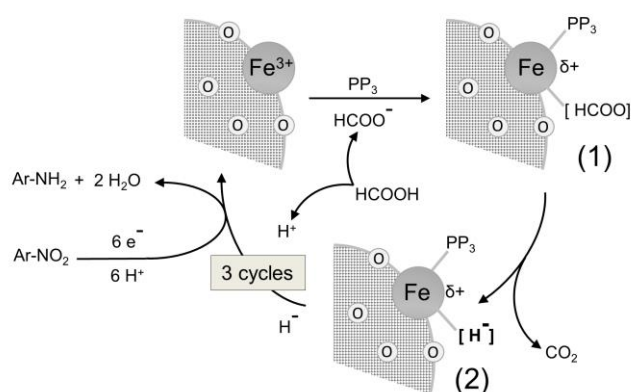
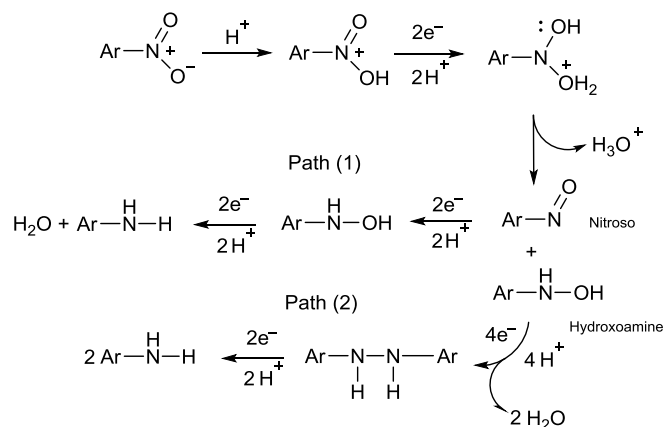


Figure 2. Schematic representation of the conversion of Ar-NO₂ to Ar-NH₂ brought by MMIO catalyst (α -Fe₂O₃), acid (HCOOH) and triphenylphosphine (PP₃). The interaction among the surface exposed Fe³⁺ cation of the α -Fe₂O₃ 3D assembly (MMIO) with HCOO⁻ and PP₃ has been highlighted by the indices (1) and (2).



Scheme 2. Possible pathways for the reduction of nitroarenes to amines.

To evaluate the reusability of the catalyst, a series of recycling experiments were conducted which revealed that synthesized iron oxide could be successfully utilized four times with no major loss of catalyst activity (Figure 3). We noticed that the initial morphology of MMIO, is nearly preserved after recyclability studies (Figure S2). In contrast to the reported protocols in the literature, which often required several hours (1-24 h) for completion, the present method required only 40 minutes. Most importantly, the method avoids the use of expensive noble metals (Pd, Pt, Au etc.), and other transition metals (Ni, Co, etc.) catalyst, and still is comparable in prowess to the existing protocols.^[19] Additionally, we also compared obtained results in present work

with the previously reported mesoporous iron-based catalysts and other some iron containing catalysts and found that our catalysts is comparable/better than previously reported catalysts (Table S1).

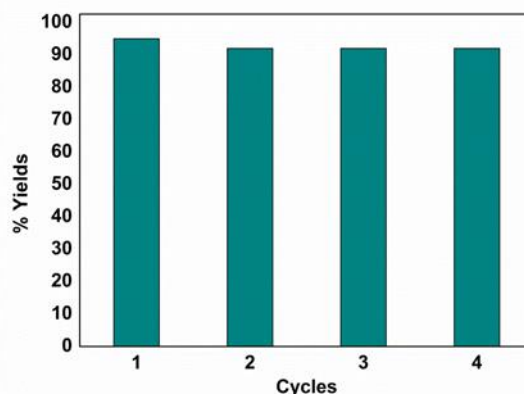


Figure 3. Reusability of MMIO: 4-nitroanisole (0.54 mmol), formic acid (5.4 mmol), catalyst (40 mg), tetraphos (12 mol%), ethanol (4 mL), 70 °C, 40 minute.

Conclusions

In conclusion, heterogeneous micro-mesoporous iron oxides (MMIO) was synthesized *via* solid-state thermal treatment of iron oxalate precursors and its catalytic performance was evaluated for the efficient reduction of aromatic nitro compounds in good to excellent yields without any additional base. The catalytic systems works in environmentally benign ethanol solvent and formic acid as a hydrogen donor to generate the corresponding anilines under mild reaction conditions. The advantage of the catalyst is that it is robust, could be produced on a large-scale and is accessible from inexpensive raw materials. Importantly, no noble or transition metals used in this protocol, which renders this protocol more benign and sustainable. We believe that the combination of micro-mesoporous iron oxides and tetraphos-based ligands could be employed for several other industrially important transfer hydrogenation reactions.

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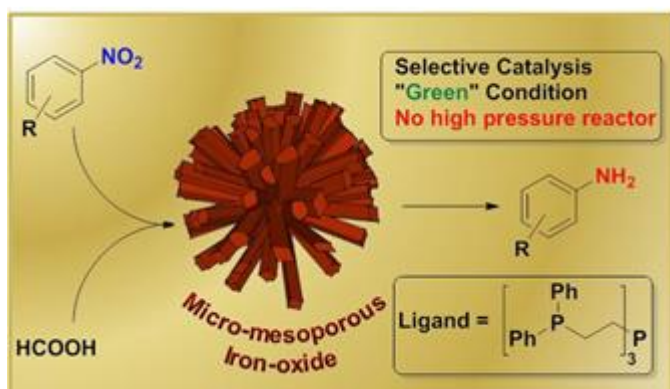
Keywords –

micro-mesoporous iron oxides, heterogeneous catalysis, reduction reactions, reusability, anilines

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Table of Content



Supporting Information

Base-free Transfer Hydrogenation of Nitroarenes Catalyzed by Micro-mesoporous Iron Oxide

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Table of content

Experimental details

Preparation of the MMIO catalyst

General procedure for the reduction of nitrobenzene

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Experimental Details

Characterization -

Field emission scanning electron microscopy (FESEM) images were taken on a Hitachi 6600 FEG microscope operating in the secondary electron mode and using an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) investigations were performed at 80 kV accelerating voltage on FEI TitanG2 60-300 transmission electron microscope equipped with X-FEG electron gun, objective-lens image spherical aberration corrector and chemiSTEM EDS detector. Nitrogen adsorption-desorption isotherms at 77 K were measured up to the saturation pressure of nitrogen (molecular cross-sectional area of 0.162 nm^2), and obtained by the static volumetric technique on an Autosorb-iQ-C analyzer (Quantachrome). Prior to the measurement, samples were degassed at room temperature for 12 h to reach pressure below 0.001 Torr. Specific surface areas were calculated using the multipoint BET (Brunauer-Emmet-Teller) model. The best fits were obtained using adsorption data in the relative pressures of 0.08-0.25 (p/p_0). The pore volumes were calculated from the amount of nitrogen adsorbed at a relative pressure of 0.95 (p/p_0). The zeta potential measurements were carried out using a Zetasizer Nano particle analyser ZEN3600 (Malvern Instruments, UK). Samples were analyzed using an Agilent 6820 gas chromatograph equipped with an Agilent DB-5 capillary column (30 m x 0.32 mm, 0.5 μm) under the operation parameters: temperature of inlet of 100 °C, temperature of flame ionization detector of 250 °C, temperature ramp of the oven from 100 to 250 °C at a rate of 10 °C min^{-1} .

Preparation of the MMIO catalyst-

In a typical synthesis, 1 mmol of oxalic acid was dissolved in 10 mL of dimethylacetamide (DMA) under continuous stirring. An equal mole ratio of aqueous iron chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$)

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solution was added to it followed by addition of oxalic acid solution and deionised water, in that order. After stirring for 10 minutes, the as synthesized yellow coloured product were separated by centrifugation and washed with ethanol five times and dried at 333 K for 12 h. Micro-mesoporous iron oxide nanostructures were obtained by the thermal decomposition of as-prepared $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in air by following procedure. The precursor, $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, was finely homogenized in an agate mortar. Next, the powdered precursor (1 g) was spread on the bottom of a crucible in a thin layer (ca. 1 mm thick) and heated in air at 448 K for 12 h.

General procedure for the reduction of nitrobenzene -

The liquid phase reductions of nitroarenes were performed in a 10 mL two-necked flask equipped with a condenser in one and another vent is closed with a septum for sample withdrawal. The whole system was kept in a thermostated oil bath attached with a magnetic stirrer coupled with a heating plate. In a typical reaction, to a stirred mixture of nitrocompound (0.27 mmol) in ethanol (2 mL) was added catalyst (20 mg) and tetrachloro ligand (6 mol%) followed by the addition of formic acid (2.7 mmol). The resulting reaction mixture was heated at 70 °C for appropriate time (Table 5) and the samples were withdrawn at regular intervals. The progress of the reaction was monitored by thin layer chromatography (silica gel; hexane/ethyl acetate) and the conversion and yield of the reaction was determined by GC using *n*-hexadecane as internal standard.

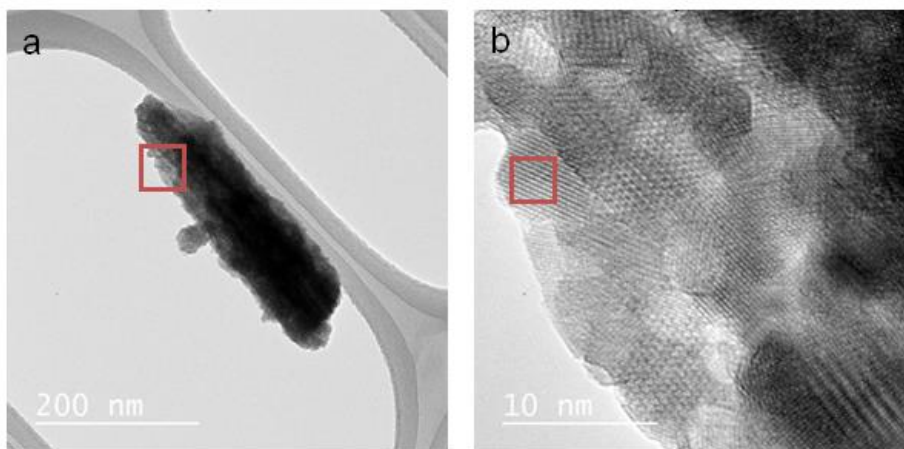


Figure S1. (a) Bright field TEM image of an individual flake of MMIO sample. (b) HRTEM image of a small section of this sample showing lattice fringes from multiple grains.

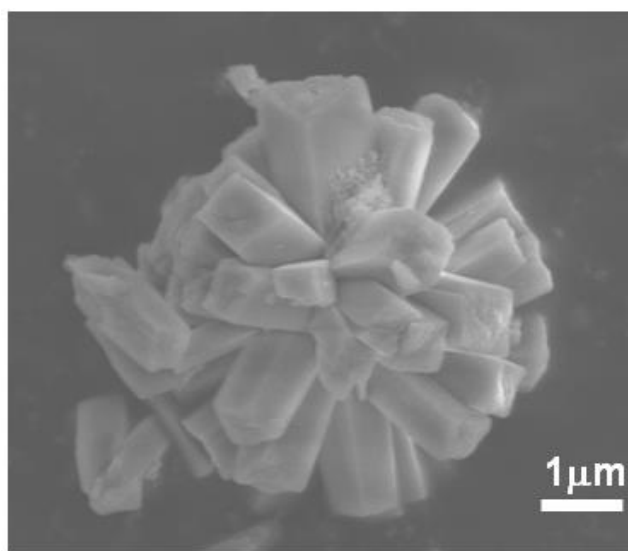


Figure S2. SEM image of MMIO after recyclability studies.

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Table S1. Comparison of selected heterogeneous/iron-based catalysts for the reduction of 4-methoxy nitrobenzene.

Entry	Catalyst	Conditions	Yield (Conversion)% ^a	Ref.
1	FeHMA Trivalent iron-HMA	FeHMA, KOH, Propoal-2-ol, 356 K, 2.5 h	88	1
2	γ -Fe ₂ O ₃ -MNAs	MeNHNH ₂ , ethanol, 60 °C, 1.5 h	97	2
		NH ₂ NH ₂ , ethanol, 60 °C, 2 h	95	
3	Iron oxide-MgO	Hydrazine hydrate, 333K, 6 h	(96)	3
4	Fe(II)Pc	Ph ₂ SiH ₂ , ethanol, 100 °C, 24 h	88	4
5	Polymer-supported hydrazine hydrate/iron oxide hydroxide	Propan-2-ol, Reflux , 50 minutes	96	5
6	MMIO	HCOOH, tetrachos, ethanol, 70 °C, 40 min.	95	Present work

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