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# COMMUNICATION

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# Iron and Nitrogen Co-doped Mesoporous Carbon-Based Heterogeneous Catalysts for Selective Reduction of Nitroarenes

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Abstract. A facile fabrication of Fe and N co-doped mesoporous carbon (MC), as an efficient heterogeneous catalyst for the highly selective reduction of nitroarenes, is described. The Fe and N co-doped MC nanosheets are easily synthesized via a hydrothermal reaction between citrate acid and magnesium citrate, followed by calcination in the presence of melamine and potassium ferrocyanide. The Fe-N complex provides a unique active site for the selective reduction of 1-chloro-4-nitrobenzene, leading to the production of (E)-1,2-bis(4-chlorophenyl)diazene with a selectivity of >96%, in <40 mins. Control experiments based on non-doped, N-doped, and Fe-doped MC nanosheets demonstrate that selectivity greatly depends on the catalyst active component type, and that non-doped MC significantly contributes to the high efficiencies observed in the selective synthesis of azoxy compound intermediates. A broad range of substrates, including extra-functional groups on the nitroarenes rings, were successfully converted to the corresponding azo compounds at mild conditions with high selectivity.

**Keywords:** Azo compounds; Azoxy compounds; Heterogeneous catalysts; Iron and nitrogen co-doping; Selective catalyzed reduction

Aromatic azo compounds are widely used as raw materials in the chemical, food and pharmaceutical industries.<sup>[1-5]</sup> For example, azo compounds are considered as promising candidates across a wide range of applications as nonlinear optics,<sup>[6,7]</sup> components,<sup>[8,9]</sup> catalytic photoregulation promoters,<sup>[10]</sup> photochemical reaction species<sup>[11]</sup> and switches.<sup>[12]</sup> photo-mechanical Primary azo compounds are generally produced by azo coupling and the Mills reaction;<sup>[10,13]</sup> however, these general synthetic methods present numerous disadvantages, such as the requirement of excess amounts of oxidants or reductants and explosive initiators, having poor selectivity, and producing environmentally noxious wastes.<sup>[10]</sup> Noble metals have recently been used as heterogeneous catalysts as an improved and alternative method to efficiently obtain azo

compounds by selectively reducing nitroarenes.[14-18] Corma and co-workers<sup>[14,15]</sup> reported a gold-catalyzed synthesis of azo compounds through a two-step, onepot reaction, under a partial pressure of hydrogen and oxygen. Zhu *et al*<sup>[16]</sup> observed that in the presence of</sup> $Au/ZrO_2$ , the catalyzed coupling of nitroarenes to the corresponding azo compounds in isopropyl alcohol, proceeded when illuminated with incandescent light or ultraviolet light. Hu et al.[17] used a catalyst comprising ultra-thin Pt nanowires to obtain azo compounds derived from their nitro counterparts. Although outstanding selectivity and yields have been achieved *via* tuning the heterogeneous catalyst and reaction conditions, the high cost of noble metal catalysts is a clear drawback, which severely prevent their industrialization.<sup>[10]</sup>

Recently, numerous non-noble metals<sup>[18–20]</sup> and carbon materials<sup>[21]</sup> have been employed as catalysts toward the selective reduction of nitroarenes that exhibit excellent selectivity and conversion efficiency. Such reports inspire the design of new, low-cost catalysts for commercialization.

Iron, as a cheap, less-toxic and earth-abundant element would be considered as an ideal catalyst if comparable selectivity and yields could be achieved. Fe<sub>3</sub>O<sub>4</sub>,<sup>[22]</sup> iron,<sup>[23,24]</sup> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-based catalysts,<sup>[25]</sup> have previously been reported to demonstrate such type of catalytic reduction. Azo compounds are formed as important intermediates, especially in the presence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, which follows a hydrogen transfer reaction pathway. Although azo compounds are thermodynamically stable through resonance, such compounds are inevitably converted to anilines on the surface of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> catalysts in the presence of hydrazine. However, challenges remain to design effective iron-based catalysts with the desired catalytic properties for the highly selective formation of azo compounds, rather than complete reduction to anilines.[22-25]

Herein, for the first time, we report Fe and N codoped mesoporous carbon materials (denoted as NMC-Fe) as effective heterogeneous catalysts for the selective catalytic reduction of nitroarenes that yield azo compounds as the final and stable products, rather than anilines.



**Figure 1.** Characterization of Fe and N co-doped mesoporous carbon materials (NMC-Fe) (the phase with the highest degree of occupied active sites): (A) scanning electron microscopy (SEM) image, (B) transmission electron microscopy (TEM) image, (C) high resolution TEM image, (D) energy-dispersive x-ray spectroscopy mappings and spectrum, (E) x-ray photoelectron spectroscopy (XPS) survey spectrum, and (F) nitrogen adsorption/desorption isotherm (inset: pore size distribution).



**Figure 2.** XPS spectra of NMC-Fe: (A) C *1s*, (B) N *1s*, (C) O *1s*, and (D) Fe *2p* regions.

The synthesis procedure of NMC-Fe is systematically detailed in the experimental section, in which the carbon precursor is prepared *via* a Mg-assisted calcination process.<sup>[26]</sup> To obtain NMC-Fe, a mixture comprising the carbon precursor, melamine and potassium ferrocyanide, at a mass ratio of 1:1:1, was subjected to calcination at 800 °C for 1 hr, under a nitrogen atmosphere. N-doped mesoporous carbon (denoted as NMC) and Fe-doped catalysts mesoporous carbon (denoted as MC-Fe) were prepared under the same conditions as that of NMC-Fe, except that no potassium ferrocyanide or melamine was added, respectively.

As-synthesized Material Characterization. Α vertically crosslinked 3D nanosheet morphology is observed in the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of NMC-Fe (Figure 1A-C), in which the (211) and (121) planes of Fe<sub>3</sub>C are suggested to be homogeneously dispersed. The nitrogen content in NMC-Fe is calculated from x-ray photoelectron spectroscopy (XPS), in Figure 1E, as 21.62 at.%. The nitrogen adsorption/desorption isotherm of NMC-Fe shows the carbon material to possess mesoporosity, having a large specific surface area of 407.8 cm<sup>3</sup>  $g^{-1}$ and mesopores with an average diameter of ~3.45 nm (Figure 1F). The nanostructures of MC, NMC and MC-Fe (Figures S1–S3) are similar, demonstrating that the nitrogen and iron doping processes are not influencing the intrinsic structure of the carbon skeleton. To determine the binding energies of each element in the MC, NMC and MC-Fe nanocatalysts, XPS was performed, Figures S4–S6. Compared with the MC-Fe catalyst (Figure S6), the Fe 2p XPS spectrum of NMC-Fe (Figure 2) indicates a change in the surface iron valence from Fe<sup>3+</sup> to Fe<sup>2+</sup>. As a result of nitrogen doping, the N 1s spectrum of NMC-Fe shows that a large fraction of pyrrolic N is converted to pyridinic N, which coordinates with  $Fe^{2+}/Fe^{3+}$  to form Fe-N complexes. Such Fe-N complexes have been successfully applied in oxygen reduction reactions for fuel cells.



**Figure 3.** X-ray diffraction patterns of the as-obtained mesoporous carbon (MC), and the N-doped MC (NMC), Fe-doped MC (MC-Fe) and NMC-Fe catalysts.

The iron content in MC-Fe and NMC-Fe were confirmed by x-ray diffraction (XRD) (Figure 3). For iron-doped MC-Fe, the lattice structure attributed to Fe<sub>3</sub>C can be detected. Conversely, for NMC-Fe, in the presence of both iron and nitrogen, both the Fe<sub>3</sub>C and Fe<sub>2</sub>O<sub>3</sub> structures can be observed. Therefore, nitrogen doping significantly influences the iron valency and can promote the formation of the Fe-N complex. Additionally, a MgO side product exists in the nanocatalysts. Figure 4 shows the Raman spectra of MC, NMC, MC-Fe and NMC-Fe. Of particular note is the intensity ratio of the D band ( $\sim 1350 \text{ cm}^{-1}$ ) to G band (~1590 cm<sup>-1</sup>), I<sub>D</sub>/I<sub>G</sub>, which determines the relative concentration of local defects or disorders. NMC-Fe exhibits a significantly smaller I<sub>D</sub>/I<sub>G</sub> ratio when compared with the non-doped MC catalyst, demonstrating that nitrogen and iron doping occupy the vacancies and defect sites in the carbon nanosheets. As a result, iron- and/or nitrogen-doped carbon catalysts exhibit a smaller surface area than the non-doped MC (as shown in Table S1).



**Figure 4.** Raman spectra of the as-obtained MC, NMC, MC-Fe and NMC-Fe materials.

Selective Reduction of Nitroarenes. In Table 1, all synthetic reactions were conducted in the presence of 1-chloro-4-nitrobenzene (1.0mmol) (1a), hydrazine hydrate (1.65 equiv.), KOH (1.5 mmol), the corresponding catalyst (43 mg), and toluene (1 mL), sealed in a 20 mL Schlenk tube, at 100 °C for 1 hr. The minimum amount of NMC-Fe catalyst, set at 43 mg, equates to 1.0 mmol 1a. Surprisingly, both Fedoped and N-doped carbon materials are able to (E)-1,2-bis(4-chlorophenyl)diazene generate (3a)from the reduction of 1,2-bis(4-chlorophenyl)diazene oxide (4a), a key intermediate catalyzed by MC as an essential pre-catalytic step. A low level of conversion was observed for 1a in the absence of the above carbon materials, suggesting that MC can be the catalyst for 4a, while Fe and N co-doped MCs alter the selectivity of this one-pot, two-step catalytic reduction of 1a to 3a. Comparison of the chemical compositions of the three carbon catalysts suggests that the as-formed NMC-Fe is responsible for the excellent observed **3a** selectivity of 96%, which for the reduction of **1a**, even outperforms noble metal catalyst systems. Conversely, only a **3a** selectivity of 21% is observed in the presence of the MC-Fe catalyst system, highlighting the importance of the co-doping of both Fe and N toward the selective reduction of **1a**. The NMC catalyst exhibits an even lower **3a** selectivity of 12%, confirming, once again, that individually doping with iron or nitrogen yields lower **3a** selectivity as a result of the inability to form the Fe-N complex.

 Table 1. Catalyst influence on 1a conversion and product yield.

4-CIPhNO <sub>2</sub> <b>1a</b>	Cat., NH <sub>2</sub> NI <sup>2</sup> KOH, Toluene	CIPhNH <sub>2</sub> + <b>2a</b>	4-CIPhN= 3a	NPhCl-4	
			+ 4-CIP	hN=N(O)F <b>4a</b>	PhCI-4
Entry <sup>a</sup>	Cat.	Conv.	Yield <sup>b</sup> (%)		
	(43mg)	(%)	2a	3a	4a
1	MC	97	4	4	89
2	NMC	100	3	12	85
3	MC-Fe	100	4	21	75
4	NMC-Fe	100	3	96	1
5	-	33	2	2	29

<sup>a)</sup> All reactions were conducted in the presence of 1-chloro-4-nitrobenzene (1.0mmol) (**1a**), hydrazine hydrate (1.65 equiv.), KOH (1.5 mmol) and the corresponding catalyst (43 mg) in toluene (1 mL), in a sealed 20 mL Schlenk tube, at 100 °C for 40 mins. <sup>b)</sup> Calculated according to the peak area from GC-MS.

Typically, a hydrogen transfer mechanism is involved in the iron-based catalyst systems.<sup>[22]</sup> The negatively charged hydride adsorbents formed during the transition are better stabilized by iron active centers (electron-withdrawing substrates). The complexes that are formed act as hydrogen transfer centers for the selective reduction of nitroarenes to azo compounds. To examine whether the NMC-Fe catalytic conversion follows a traditional one-step hydrogen transfer mechanism,<sup>[22]</sup> or a newly proposed two-step, azoxy compound-mediated type of catalysis,<sup>[17]</sup> the catalyzed-reduction of nitroarenes, in the presence of NMC-Fe, was performed as a function of temperature, as shown in Table 2.



**Scheme 1.** Catalyzed reaction pathway as a function of carbon catalyst composition.

The activation threshold of NMC-Fe is apparent at a reaction temperature >40 °C. Below this critical temperature, NMC-Fe remains inactive, yielding **4a** as the main product. The plausible reaction

$4$ -CIPhNO <sub>2</sub> $\xrightarrow{\text{NMC-Fe, NH_2NH_2.H_2O}}$ $4$ -CIPhNH <sub>2</sub> + 4-CIPhN=NPhCI-4+ 4-CIPhN=N(O)PhCI-4							
	1a <sup>-</sup> KOH, Toluen	e, Temp.	2a -	3a	4a (		
Entrya	NH <sub>2</sub> NH <sub>2</sub> ·H <sub>2</sub> O	T (°C)	Conv.	Sel. (%) <sup>b</sup>			
Enuy	(equiv.)		(%)	2a	<b>3</b> a	<b>4</b> a	
1	1.65	120	100	7	90	3	
2	1.65	100	100	5	94	trace	
3	1.65	80	100	3	85	12	
4	1.65	60	100	2	70	28	
5	1.65	40	100	3	49	48	
6	2.00	100	100	15	84	trace	
7	1.75	100	100	9	91	trace	
8	1.70	100	100	7	93	trace	
9	1.60	100	100	5	91	4	
10	1.55	100	100	3	69	28	
11	1.50	100	100	2	46	52	

Table 2. Influence of temperature and hydrazine hydrate concentration.

NMC-Fe, NH<sub>2</sub>NH<sub>2</sub>.H<sub>2</sub>O

<sup>a)</sup> All reactions were performed in the presence of 1a (1.0 mmol), hydrazine hydrate, KOH (1.5 mmol) and NMC-Fe (43 mg) in toluene (1 mL), in a sealed 20 mL Schlenk tube, for 1 hr.<sup>b)</sup> Calculated according to the peak area from GC-MS.



Figure 5. Reaction dynamics of the 1a-catalyzed reduction by: (A) MC, (B) NMC, (C) MC-Fe, (D) NMC-Fe materials. -Conv%, **▼**-4a, **▲**-3a, **●**-2a.

pathways are also confirmed by varying the hydrazine hydrate concentration (Table 2). At a relatively low concentration of hydrazine hydrate (1.50 equiv.), selectivity is poor with 52% 4a remaining in the system, likely as result of the active sites not being fully occupied by hydrazine adsorbents. Increasing the concentration of hydrazine hydrate (to 1.55 equiv.) results in an additional 23% conversion of 4a to 3a. The minimum requirement of hydrazine hydrate (1.60 equiv.) must be exceeded to ensure a high selectivity of 3a, for example, 91%. Further increasing hydrazine hvdrate the concentration has a minimal effect on the selectivity and yield of **3a**. The reaction temperature has a greater influence on the final product composition. For example, aniline begins to emerge at 120 °C, as a result of the decomposition of 4a. Overall, the catalyzed-reaction pathway in the presence of NMC-Fe appears to follow the two-step, azoxy compoundmediated, one-pot selective reduction, as proposed in Scheme 1.

Figure 5A–D shows that all four carbon catalysts

exhibit a high level of 4a production at a very initial time-on-stream, ranging from 40% to 70%, strongly indicating the catalytic role of the MC support. The intrinsic zero-order reaction is also consistent with the nature of the surface reaction on a catalyst. Notably, Figure 5D reveals a ~96% 3a yield at a reaction time of <40 mins. Table 3 and Table 4 demonstrate the general applicability of this MCbased catalytic system, in which various nitroarenes, especially for halide-containing substrates, were selectively reduced to azo compounds or azoxy compounds with good-to-excellent yields and selectivity, respectively. Furthermore, aryl halides in the *meta* and *para* positions can undergo nucleophilic aromatic substitution reactions, further facilitating the formation of azo compounds. H<sup>1</sup>-NMR, C<sup>13</sup>-NMR, and GC-MS characterizations, together with references to all studied azo compounds, are listed in the Supporting Information.

**Table 3.** Fe and N co-doped mesoporous carbon (NMC-Fe)-catalyzed reductive coupling of nitroarenes to yield the corresponding symmetric azo compounds.



All reactions were performed in the presence of nitroarenes (1.0 mmol),  $NH_2NH_2 \cdot H_2O$  (1.65 equiv.), KOH (1.5 equiv.) and NMC-Fe (43 mg) in toluene (1 mL), in a sealed 20 mL Schlenk tube, at 100 °C for 1 hr. Values represent isolated yields.

Catalyst recycling stability is an important factor to evaluate the overall performance of heterogeneous catalysts. NMC-Fe was subjected to continuous operation to study the activity in a series of recycling experiments. As shown in the Figure 6C–D, the

**Table 4.** Mesoporous carbon (MC)-catalyzed reductive coupling of nitroarenes to yield the corresponding symmetric azoxy compounds.



All reactions were performed in the presence of nitroarenes (1.0 mmol),  $NH_2NH_2 \cdot H_2O$  (1.65 equiv.), KOH (1.5 equiv.) and MC (43 mg) in toluene (1 mL), in a sealed 20 mL Schlenk tube, at 100 °C for 1 hr. Values represent isolated yields.



**Figure 6.** Recycling experiments for (A) NMC-Fe (43 mg) and (B) MC (43 mg), 40 mins for each recycle. Reaction conditions: 1-chloro-4-nitrobenzene (1.0 mmol), NH<sub>2</sub>NH<sub>2</sub>·H<sub>2</sub>O (1.65 mmol), KOH (1.5 mmol), toluene (1mL), 100 °C, determined by GC. Magnetic separation or NMC-Fe. NMC-Fe before (C) and after (D) magnetic separation.

NMC-Fe catalyst can be recovered from the system experiments after the reaction using magnets. The results in Figure 6A show that a good conversion rate and selectivity were maintained for the first three recycles, however, after successive recycles thereafter, the selectivity toward azo and azoxy compounds reduced. According to Table S2, Figure 2D and Figure S8d, the reason for the decline in catalytic activity after the recycling reactions is that the proportion of surface iron in NMC-Fe decreases, with a concomitant increase in the Fe<sub>2</sub>O<sub>3</sub> content. Similar recycling experiments were performed under continuous operation to study the catalytic activity of MC. The results in Figure 6B show that after performing eight recycle experiments, a good conversion rate and selectivity were maintained, which indicated that the stability of MC was very good.

In summary, novel Fe and N co-doped MC materials are presented that demonstrate their potential for the reduction of nitroarenes to azo compounds, with a good-to-excellent yields and selectivity. To the best of our knowledge, this is the first example demonstrating that self-designed MCs can function as an iron catalyst substrate, and act as a catalyst for the selective synthesis of azoxy compounds. The highest selectivity of 96% for the conversion of azoxy compounds to azo compounds is suggested to be related to the existence of the Fe-N complex in the NMC-Fe catalyst. This cheap, fast and efficient, two-step, one-pot catalytic process can be used as a platform to provide a new synthetic method for the selective production of azoarenes.

#### **Experimental Section**

General remarks all nitroarenes were purchased from Aladdin. All reagents were used without further purification. SEM was performed using a Nova 200 Nano instrument. TEM and high-resolution TEM were performed using a JEOL-2100 instrument. XPS was performed on a spectrometer from Kratos Axis Ultradld, using mono AlKa (1486.71 eV) radiation, at a power of 120 W (8 mA, 15 kV). XRD was conducted on a Bruker D8 Advance diffractometer using CuK $\alpha$  radiation ( $\lambda = 0.15406$  nm), with the data collected across a  $2\theta$  range of  $20-80^\circ$ . The Brunauer-Emmett-Teller surface areas of the samples were measured by nitrogen adsorption using а Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). Raman spectroscopy (JY-T643200, France) was conducted at ambient conditions using a 514 nm laser excitation. Column chromatography was performed with silica gel (300-400 mesh). NMR spectra were collected on either 300 or 500 MHz spectrometers at ambient temperatures in CDCl<sub>3</sub>. Chemical shifts are given in parts per million (ppm) with respect to tetramethylsilane (0 ppm). The reaction progress was monitored by thin-layer chromatography (TLC) and/or GC-MS (Agilent 9870). Melting points were recorded on Digital Melting Point Apparatus WRS-1B and are uncorrected.

**Preparation of MC Materials.** All reagents were purchased from commercial suppliers and used without further purification. Citrate acid (0.04 mol) and magnesium citrate (0.02 mol) were dissolved in 20 mL double-distilled water, ultrasonicated for 10 mins, and thereafter, heated to 120 °C for 24 hrs, to obtain yellow precipitates, which were subjected to calcination in a horizontal tube furnace at 800 °C, at a rate of 5 °C/min<sup>-1</sup>, under a nitrogen atmosphere for 1 hr. The resulting black composites were obtained and denoted as the MC support.

**Synthesis of NMC, MC-Fe and NMC-Fe.** The catalysts were all prepared using various compositional mixtures containing the carbon precursor, MC. For NMC, a MC melamine mixture having a 1:1 wt.% ratio was used. A carbon precursor, MC, and potassium ferrocyanide mixture having a 1:1 wt.% ratio of MC melamine and potassium ferrocyanide was used for NMC-Fe. A 1:1:1 wt.% ratio of MC, melamine and potassium ferrocyanide was used for NMC-Fe. All mixtures were subjected to heating at 800 °C for 1 hr.

General Synthetic Procedure for Azo Compounds Nitroarenes (1 mmol), hydrazine hydrate (1.65 mmol), KOH (1.5 mmol), and the catalyst (NMC-Fe, 43 mg) were mixed in toluene (1 mL), in a sealed 20 mL Schlenk tube, under an air atmosphere, and stirred at 100 °C for 1 hr. The reaction progress was monitored by TLC and/or GC-MS. After completion, the product was purified by column chromatography using ethyl acetate and petroleum ether as the eluents. General Synthetic Procedure for Azoxy **Compounds.** The synthetic procedure for the formation of azoxy compounds followed that of the azo compounds except for substitution of NMC-Fe with MC.

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