

# Synthesis and Characterization of Iron-Nitrogen-Doped Graphene/Core-Shell Catalysts: Efficient Oxidative Dehydrogenation of *N*-Heterocycles

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**ABSTRACT:** An important goal for nano-catalysis is the development of flexible and efficient methods for preparing active and stable core-shell catalysts. In this respect, we present the synthesis and characterization of iron oxides surrounded by nitrogen-doped-graphene shells immobilized on carbon support (labelled FeO<sub>x</sub>@NGr-C). Active catalytic materials are obtained in a simple, scalable and two-step method via pyrolysis of iron acetate and phenanthroline and subsequent selective leaching. The optimized FeO<sub>x</sub>@NGr-C catalyst showed high activity in oxidative dehydrogenations of several *N*-heterocycles. The utility of this benign methodology is demonstrated by the synthesis of pharmaceutically relevant quinolines. In addition, mechanistic studies prove that the reaction progresses via superoxide radical anions ( $\cdot\text{O}_2^-$ ).

## INTRODUCTION

Since the past decade, there exists an increasing interest in the development of iron-based organometallic catalysts for organic synthesis.<sup>1</sup> The inherent advantages of these complexes such as ready availability, low toxicity and environmental friendliness, make them preferred candidates for catalysis.<sup>2</sup> However, it should be noted that research on iron compounds has a long tradition; in fact, this is one of the oldest fields in chemistry and iron is also used widely and successfully in heterogeneous catalysis since the beginning of the last century.<sup>3</sup> In recent years, especially iron-based nanoparticles came into the focus of researchers because they feature novel properties different from the corresponding bulk materials.<sup>4</sup> Unfortunately, most of today's known highly active nano-iron catalysts are unstable and they are easily deactivated because of aggregation or leaching of the active metal in the reaction mixture. The development of core-shell structured materials provides a possibility to solve these problems. In case of iron nanoparticles, the resulting materials are often protected by organic or inorganic shells,<sup>5</sup> usually prepared at low temperature,<sup>6</sup> which limits the preparation and application of potential nano-catalyst.

Recently, iron-nitrogen-carbon (Fe/N/C) catalysts prepared by thermolysis of iron-ligated amines immobilized on high surface area have been studied in electro-catalysis, photocatalysis and organic synthesis.<sup>4c,7</sup> For these catalysts, *N*-doped materials are demonstrated to produce defects in graphene stacking in carbon based catalysts, which result in the formation of the O<sub>2</sub> absorption active sites. Interestingly, the activity of such Fe/N/C materials can be tuned by the choice of nitrogen precursor, the iron species, the carbon support morphology and the pyrolysis temperature.<sup>8</sup> Meanwhile, the *N*-doped graphene like materials have the ability to reductively

adsorb O<sub>2</sub> and have been employed in the catalytic reduction of nitroarenes and also for reductive aminations.<sup>9</sup> Very recently, *N*-doped carbon based catalysts are applied in the selective oxidation of alcohols and amines, too.<sup>10</sup> To the best of our knowledge, related oxidative dehydrogenations have not been investigated yet.

The catalytic dehydrogenation of *N*-heterocycles constitutes a fundamental process in organic synthesis. In recent years, several homogeneous catalysts were successfully employed in the catalytic dehydrogenations of *N*-heterocycles such as Ir-Pincer, Fe-Pincer, Ru-hydride complexes and so on.<sup>11</sup> On the other hand, heterogeneous catalysts such as Pd-HAP and CuAl-HT, have also been used for these reactions.<sup>12</sup> Stahl et al. reported a homogeneous Ru-Co catalyst for the oxidation of *N*-heterocycles and Pd-catalyzed the aerobic oxidation of cyclohexenes to aromatic arenes.<sup>13</sup> Furthermore, some heterogeneous oxidative systems such as Pd<sub>3</sub>Pb, Pt-NW, AuNPs/C, Ru/Al<sub>2</sub>O<sub>3</sub>, Ru/Co<sub>3</sub>O<sub>4</sub> and Ru/TiO<sub>2</sub> have been developed for these reactions.<sup>14</sup> However, most of the latter catalytic systems are based on noble metals or require harsh conditions and showed only poor functional-group tolerance. Thus, the development of inexpensive, earth copious and less toxic iron catalysts with a general and efficient activity for the dehydrogenation of *N*-heterocycles is still challenging and of actual interest.

Inspired by the properties of the *N*-doped graphene materials to activate O<sub>2</sub> and encouraged by our recent investigations on the use of iron-based catalysts and of *N*-doped heterogeneous materials,<sup>9,15</sup> we started to explore the preparation of novel iron-graphene materials and their application in the catalytic dehydrogenation of *N*-heterocycles. Herein, we report the preparation of novel iron oxide nanoparticles surrounded by a nitrogen-doped graphene shell supported on carbon

(FeO<sub>x</sub>@NGr-C) and describe for the first time their high stability and activity in catalytic oxidations of *N*-heterocycles.

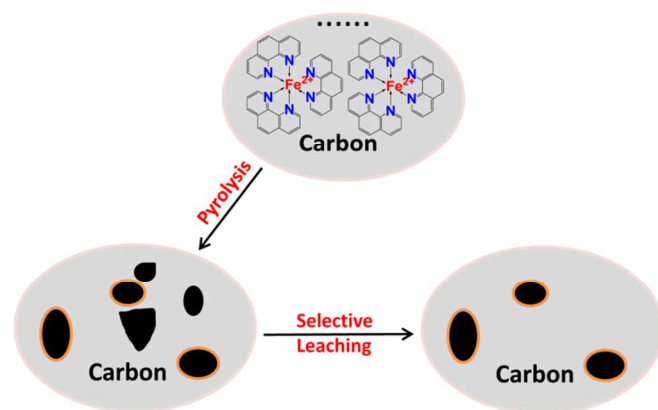


Figure 1. Schematic illustration showing the general procedure for the synthesis of FeO<sub>x</sub>@NGr-C.

## RESULTS AND DISCUSSION

Typically, this new type of FeO<sub>x</sub>@NGr-C catalyst was prepared using iron acetate, as the iron precursor and 1,10-phenanthroline (L1) as the nitrogen-rich ligand and the graphene precursor. Figure 1 and 2 depicts the general preparation of the FeO<sub>x</sub>@NGr-C catalyst. Using ethanol as the solvent the formation of the iron complex and its uniform adsorption on the carbon support is facilitated. We suppose that the structure of the resulting immobilized metal-coordination polymer prevents the iron sites from agglomeration during the high temperature treatment and is favorable for the formation of well dispersed highly active sites. Moreover, the scaffold of 1,10-phenanthroline is relatively thermally stable, promoting the formation of graphene-like materials during pyrolysis (>600 °C). Variation of the temperature revealed that precursor was most effectively pyrolyzed at 800 °C for 2 h under Ar. Subsequent treatment with aqueous HCl solution overnight selectively removed inactive, agglomerated and unprotected iron particles generated during the pyrolysis process.

Structural characterization of the FeO<sub>x</sub>@NGr-C system was carried out using various methods as shown in Figure 3. Obviously, larger iron nanoparticles were removed after selective leaching with HCl solution and only small nanoparticles (20-30 nm) remained (Figure 3a and Figure S 1). As expected, high-resolution transmission electron microscopy (HRTEM) image revealed that all present nanoparticles were protected by graphene shells (Figure 3b and Figure S2). More specifically, 3-12 layers are observed which correspond to a thickness of 1.2-3.5 nm. Interestingly, some carbon nanotubes were observed on the surface, too. Most likely, the latter are left behind after removing the larger iron particles which cannot be protected well by the graphene shells (Figure S3). The iron/graphene core-shell structure was further proved by HAADF images. It is worth noting that the core shell structure remained intact after using the catalyst for several times



Figure 2. Schematic illustration for the preparation of the FeO<sub>x</sub>@NGr-C. (a) Photograph of the Fe-phen complex. (b) Photograph of the catalyst precursor before pyrolysis. (c) Photograph of the obtained FeO<sub>x</sub>@NGr-C.

demonstrating the stability of the FeO<sub>x</sub>@NGr-C architecture (Figure S4). From the XRD analysis, the broad reflections at about 25° and 44° are from the C-support (Figure S5). In addition, a sample pyrolyzed at higher temperature (1000°C) showed sharper reflections caused by the crystalline phase Fe<sub>3</sub>C and a small amount of FeN. XPS analysis revealed that the content of carbon grew with increasing the pyrolysis temperature, whereas the content of N and Fe decreased due to the high temperature (Table S2). The content of the Fe dropped from 0.36% to 0.17% as the pyrolysis temperature increased from 600 °C to 800 °C, suggesting that higher pyrolysis temperature faster the agglomeration. However, increasing the temperature to 1000 °C left the content of iron almost unchanged. The peaks in the N1s spectrum at 398.9 eV and 400.9 eV are assigned to pyrrolic N and graphitic N on the basis of the respective binding energies (Figure 3d). It is reported that the graphitic N plays a crucial role in the oxygen reduction,<sup>10d</sup> which might explain the high activity of the FeO<sub>x</sub>@NGr-C catalyst. In addition, Fe<sup>2+</sup> and Fe<sup>3+</sup> were detected according to the corresponding binding energies at 710.2 eV, 716.0 eV, 722.1 eV and 726.1 eV after pyrolysis at 800 °C.

In order to examine the activity of the prepared catalysts for selective oxidative dehydrogenation of heterocycles, we initially tested different FeO<sub>x</sub>@NGr-C materials with 1,2,3,4-tetrahydroquinoline as the model substrate. As shown in Table 1, FeO<sub>x</sub>@NGr catalysts with or without aqueous HCl treatment gave similar product yield (Entries 1 and 2). However, the pyrolyzed catalyst which was washed subsequently with aqueous HCl achieved higher TONs (267 and 106 mol/mol Fe, respectively). Compared to the non-washed catalyst no by-products, such as quinolinone, were detected by GC and GC-MS analysis and full selectivity for the desired product was obtained. The better selectivity of the HCl-treated catalyst is

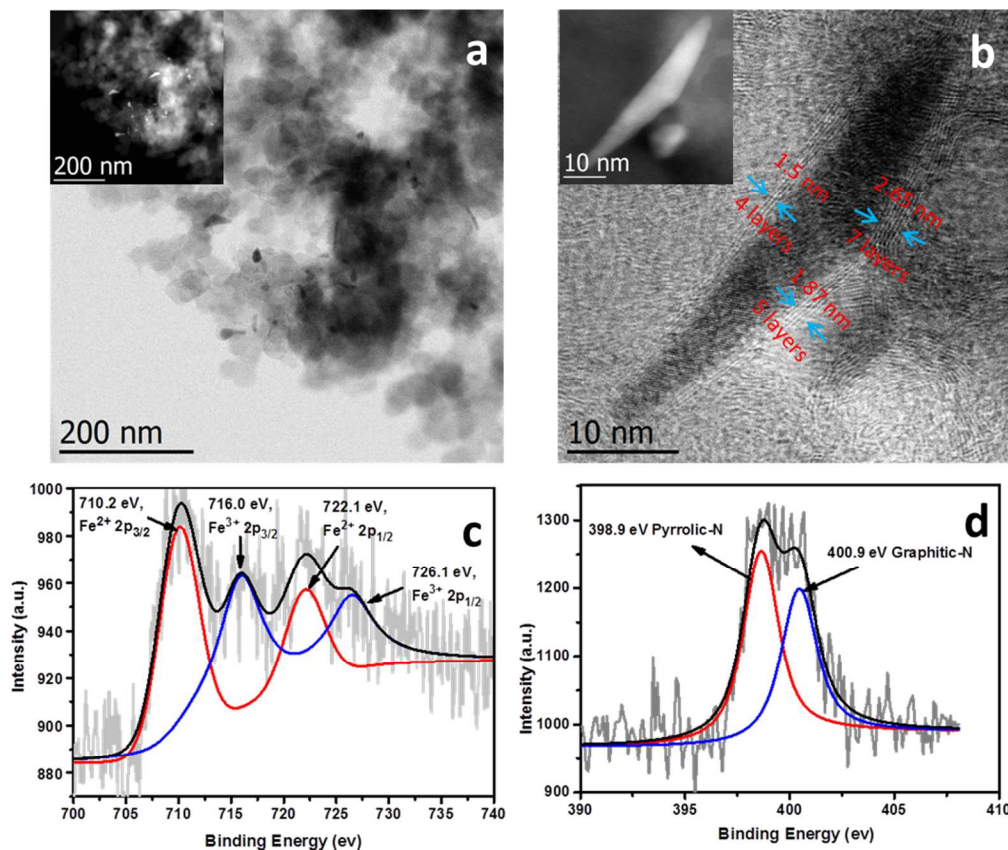
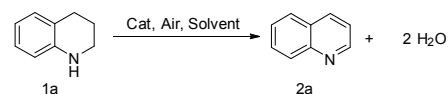


Figure 3. HRTEM images (a and b) of the  $\text{FeO}_x@\text{NGr-C}$  (Inset of a and b: HAADF images), Fe 2p XPS spectrum (c) and N 1s XPS spectrum (d) of  $\text{FeO}_x@\text{NGr-C}$ .

attributed to the specific structure of  $\text{FeO}_x@\text{NGr-C}$  material, in which all the catalytically active iron species are confined with the graphene capsule. Apparently, this specific structure inhibits the interaction of the  $\text{CH}_2$  group of 1,2,3,4-tetrahydroquinoline with the active site of the catalyst, so the formation of quinolinone is avoided. In contrast, without HCl washing larger iron oxide nanoparticles are present at the surface, which show unspecific reactivity. As a control reaction, the carbon-supported iron oxide, i.e.  $\text{FeO}_x/\text{C}$ , was prepared in the absence of **L1** and lower activity was observed in the dehydrogenation reaction of 1,2,3,4-tetrahydroquinoline (Entry 3). Pyrolysis of bare carbon and **L1** exhibited poor activities in the oxidation of 1,2,3,4-tetrahydroquinoline, too (Entries 4 and 5). Notably, using  $\text{SiO}_2$  and  $\text{CeO}_2$  as supports gave also active materials, albeit the reactivity is somewhat lower (yields of quinolone: 23% and 21%, respectively; Entries 6 and 7).

**Table 1. Model Reaction: Study of Reaction Conditions<sup>a</sup>**



Entry	Catalyst	Solvent	Con(%)	Y (%) <sup>b</sup>	TON
1	$\text{FeO}_x@\text{NGr-C-NL}$	$\text{CH}_3\text{CN}$	63	46	106
2	$\text{FeO}_x@\text{NGr-C}$	$\text{CH}_3\text{CN}$	48	48	267
3	$\text{FeO}_x/\text{C}$	$\text{CH}_3\text{CN}$	17	15	5

4	C	$\text{CH}_3\text{CN}$	13	10	--
5	L1/C	$\text{CH}_3\text{CN}$	6	4	--
6	$\text{Fe/L1/SiO}_2$	$\text{CH}_3\text{CN}$	24	23	7
7	$\text{Fe/L1/CeO}_2$	$\text{CH}_3\text{CN}$	21	21	6
8	$\text{FeO}_x@\text{NGr-C}$	$\text{H}_2\text{O}$	18	18	100
9	$\text{FeO}_x@\text{NGr-C}$	$\text{CH}_3\text{OH}$	38	37	205
10	$\text{FeO}_x@\text{NGr-C}$	Toluene	40	39	217
11	$\text{FeO}_x@\text{NGr-C}$	Xylene	36	36	200
12	$\text{FeO}_x@\text{NGr-C}$	Heptane	75	74	411
13	$\text{FeO}_x@\text{NGr-C}$	Heptane	44	43 <sup>c,d</sup>	239
14	$\text{FeO}_x@\text{NGr-C}$	Heptane	85	85 <sup>c</sup>	472
15	$\text{FeCl}_2 + \text{L1/C}$	Heptane	0	10 <sup>c</sup>	5
16	$\text{FeCl}_3 + \text{L1/C}$	Heptane	0	7 <sup>c</sup>	4
17	$\text{FeO}_x@\text{NGr-C}$	Heptane	100	77 <sup>e</sup>	427
18	$\text{FeO}_x@\text{NGr-C}$	Heptane	100	83 <sup>f</sup>	461

<sup>a</sup>Reaction conditions: 0.5 mmol 1,2,3,4-tetrahydroquinoline, 30 mg catalyst (0.18 mol% Fe, 10 bar air, 2 mL solvent, 100 °C, 12 h, NL = No Leaching. For entries 15 and 16, 1.0 mol% Fe and 30 mg L1/C were used. <sup>b</sup>The yields were obtained by GC using dodecane as internal standard. <sup>c</sup>15 bar air. <sup>d</sup>80°C. <sup>e</sup>20 bar air. <sup>f</sup>8%  $\text{O}_2$  in  $\text{N}_2$ , 40 bar. Warning: the upper flammable limit for heptane is 6.7%, the reaction was operated far away from igniting sources.

Next, different solvents were tested in the model reaction. In general, nonpolar solvents gave higher yields and the best yield (74%) was obtained when using heptane as solvent (Entries 8-12). When the reaction temperature decreased to 80 °C, high selectivity but lower activity is detected (Entry 13). On the other hand, the catalytic activity is improved (85% yield) by increasing the air pressure to 15 bar (Entry 14). We also tested the catalytic activity of FeCl<sub>2</sub> and FeCl<sub>3</sub> as catalyst precursors in the presence of the N-doped carbon, which are likely to be formed during the leaching procedure and absorbed on the catalyst. In this context, the activities were very low (Table 1, Entries 15 and 16). Increasing the air pressure to 20 bar, the yield was decreased to 77% because quinolone was detected (Entry 17). When the reaction was carried out with diluted O<sub>2</sub>, 83% yield was obtained (Entry 18). Furthermore, the pyrolysis temperature was varied in the range between 600 °C and 1000 °C, and the corresponding results suggest that 800 °C is the optimized temperature (Table S1, Entries 1 and 2). Interestingly, when L2-L5 were chosen as ligands instead of L1, 6-49% yield of quinoline was observed under the same reaction conditions (Table S1, Entries 3-7).

In heterogeneous catalysis, it is still challenging to avoid the aggregation and leaching of the active metal during the reaction, which often results in deactivation of the catalysts. So the reusability of our NGr-modified catalyst (FeO<sub>x</sub>@NGr-C) in the dehydrogenation of 1,2,3,4-tetrahydroquinoline was tested. For this purpose the active material was separated from the reaction mixture via simple centrifugation, and reused directly for 5 times. To our delight no obvious deactivation was observed. The yield of the desired product amounted to 79% at the 5th cycle and the total TONs were 2317 (Figure 4). Additionally, no further reaction was observed, when the catalyst was filtered off and another portion of substrate was added. Hence, the catalytically active species should not be derived from the leached metals.

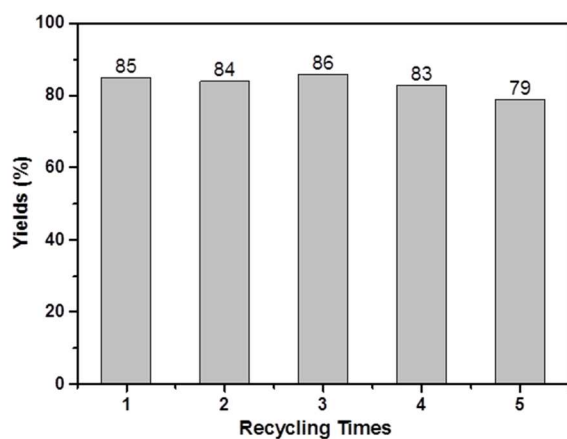


Figure 4. Oxidation of 1,2,3,4-tetrahydroquinoline: recycling of the FeO<sub>x</sub>@NGr-C catalyst. Reaction conditions: 0.5 mmol substrate, 30 mg catalyst (0.18 mol% Fe), 2 mL heptane, 15 bar air, 100 °C, 12 h. Yields were determined by GC.

Since FeO<sub>x</sub>@NGr-C displayed the best activity for the production of quinoline, it was deployed in the scope study under the optimized conditions. As shown in Table 2, substitutions at the 3 and 4 positions are well tolerated, and 3-methylquinoline (**2b**) and 4-methylquinoline (**2c**) were pro-

duced with 77% and 85% yields, respectively (Entries 2 and 3). However, more sterically hindered functional groups, such as 2-methyl, 2-phenyl and 2-tetrahydroquinoline derivatives (**1d-f**), were converted to the corresponding quinolines in 51%-67% yields (Entries 4-6). As expected, higher yields were obtained using FeO<sub>x</sub>@NGr-C-NL as catalyst. Substituted quinolines at the 6 position on the aromatic ring were obtained in high yields, too. Electron-donating groups such as methoxy, ester and methyl (**1g-i**) had no significant influence on the activity of this catalytic system (Entries 7-9).

Similarly, substrates bearing electron-withdrawing functional groups were also active. Thus, 6-bromoquinoline (**2j**) and 6-chloroquinoline (**2k**) were obtained in 85% and 88% yields (Entries 10 and 11). Gratifyingly, products containing more-electron-withdrawing groups such as quinolone-6-carboxylic acid (**2l**), 6-nitroquinoline (**2m**) and 6-trifluoromethylquinoline (**2n**) were isolated in yields up to 89% (Entries 12-

Table 2. Oxidation of Tetrahydroquinolines catalyzed by FeO<sub>x</sub>@NGr-C<sup>a</sup>

Entry	Substrates	Products	Y (%) <sup>b</sup>
1			83
2	(1a)	(2a)	77
3	(1b)	(2b)	85
4	(1c)	(2c)	67 (74)
5	(1d)	(2d)	63 (77)
6	(1e)	(2e)	51 (71)
7	(1f)	(2f)	81
8	(1g)	(2g)	89
9	(1h)	(2h)	84
10	(1i)	(2i)	85
11	(1j)	(2j)	88
	(1k)	(2k)	

12			85 <sup>c</sup>
13			89 <sup>c</sup>
14			84
15			88
16			69
17			93 <sup>c</sup>
18			88
19			84
20			75
21			54
22			62
23			70

<sup>a</sup>Reaction conditions: 0.5 mmol substrate, 30 mg catalyst (0.18 mol% Fe), 2 mL heptane, 15 bar air, 100 °C, 12 h. The yields in parentheses were obtained using FeO<sub>x</sub>@NGr-C-NL. <sup>b</sup>Isolated yields. <sup>c</sup>CH<sub>3</sub>CN as solvent, 24 h.

14). Different groups at 8-position of the aromatic ring (**1o-1q**) did not exert a marked influence on the outcome of the reaction as all of the starting materials gave good to excellent yields (Entries 15-17). In addition, 2,6-, 2,7- and 2,8-disubstituted substrates with different functional groups (**1r-1u**) were also tested and the desired products were generated in 54-85% yield (Entries 18-21). Remarkably, 4,7-dichloro-1,2,3,4-tetrahydroquinoline (**1v**) was also successfully converted to the corresponding quinoline with 69% yield (Entry 22). Boron-containing compounds are important motifs in life sciences, so **1w** was tested as starting material (Entry 23). Interestingly, 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinoline (**2w**) was successfully synthesized in 70% yield.

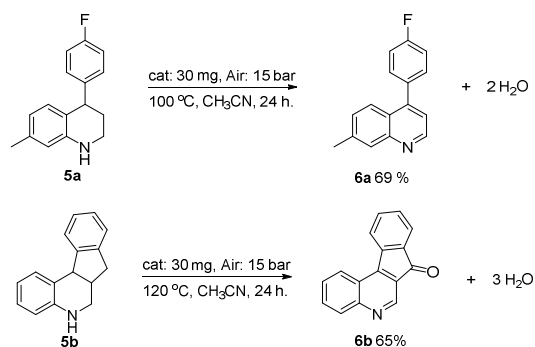
**Table 3. Oxidation of *N*-Heterocycles Catalyzed by FeO<sub>x</sub>@NGr-C<sup>a</sup>**

Entry	Substrates	Products	Y (%) <sup>b</sup>
1			83
2			78
3			87
4			93
5			79
6			92

<sup>a</sup>Reaction conditions: 0.5 mmol substrate, 30 mg catalyst (0.18 mol% Fe), 2 mL heptane, 15 bar air, 100 °C, 12 h. <sup>b</sup>Isolated yields.

Meanwhile, as shown in Table 3 the FeO<sub>x</sub>@NGr-C catalyst displayed good activity in the oxidative formation of 1,2,3,4-tetrahydro-1,10-phenanthroline (**4b**) from 1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline (Entry 2). Apart from quinoline derivatives, quinoxaline (**4a**), acridine (**4c**), quinoxaline (**4d**), isoquinoline (**4e**) and indole (**4f**) were also generated in 85%-93% yield under optimized reaction conditions (entries 1, 3-6).

**Scheme 1. Synthesis of Pharmaceutical Relevant Intermediates 6a and 6b.**



The high reactivity of the tetrahydroquinoline derivatives encouraged us to test the FeO<sub>x</sub>@NGr-C catalyst for the dehydrogenation of selected interesting bio-active compounds. As an example, the intermediate in the synthesis of the nM5-lipoxygenase inhibitor, **6a** was obtained in 69% isolated yield. Moreover, both dehydrogenation and oxidation of the benzylic group occurred when **5b**<sup>13a</sup> was employed as substrate and **6b** is obtained in 65% yield. This heterocycle is an important motif in numerous biologically active compounds (Scheme 1 and Scheme S1).



Furthermore, the selective oxidation of amines was also examined using the  $\text{FeO}_x\text{@NGr-C}$  catalyst. As shown in Table 4, the dehydrogenations of *N*-benzylaniline and *N*-butylaniline occurred smoothly and the corresponding imines are obtained in 75% and 81% yield, respectively. In addition, dibenzylamine was converted to the desired product in 83% yields.

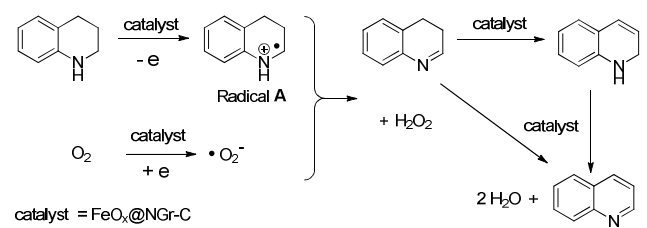
**Table 4. Oxidation of Amines Catalyzed by  $\text{FeO}_x\text{@NGr-C}^a$**

Entry	Substrate	Product	Y (%) <sup>b</sup>
1			75
2			81
3			83

<sup>a</sup>Reaction conditions: 0.5 mmol substrate, 30 mg catalyst (0.18 mol% Fe), 2 mL heptane, 15 bar air, 100 °C, 12 h. <sup>b</sup>GC yields.

In order to get insights into the mechanism of the  $\text{FeO}_x\text{@NGr-C}$ -catalyzed dehydrogenation of heterocycles, the oxidation of 1,2,3,4-tetrahydroquinoline in the presence of butylated hydroxytoluene (BHT) was investigated. Notably, in the presence of this radical scavenger, no quinoline was formed; suggesting that the reaction progressed by radical species, e.g. the superoxide radical anion ( $\cdot\text{O}_2^-$ ). It is well known that BHT can suppress the formation of  $\cdot\text{O}_2^-$ .<sup>10c,10d</sup> We assume that under catalytic conditions the nitrogen-doped graphene-like carbon materials are able to reduce absorbed  $\text{O}_2$  to  $\cdot\text{O}_2^-$ . Despite several trials the generation of  $\text{H}_2\text{O}_2$  was never observed; hence, we assume that  $\text{H}_2\text{O}_2$  is quickly consumed on forming quinoline and water (Scheme 2). Furthermore, EPR analysis revealed the formation of radical A (Figure S6), which is in agreement with the proposed catalytic pathway. In addition, the used  $\text{FeO}_x\text{@NGr-C}$  was analyzed by XPS. Interestingly, the content of  $\text{Fe}^{3+}$  is decreased and binding energies for  $\text{Fe}^{2+}$  are moved to 710.8 eV and 723.9 eV, which suggests that the synergism between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  species influences the activity during the reaction (Figure S7).

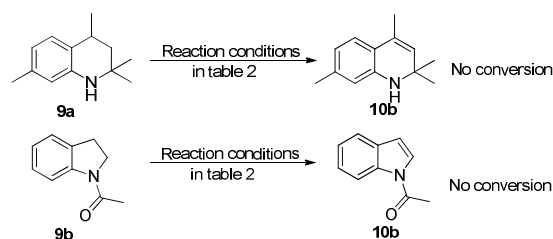
**Scheme 2, Proposed Catalytic Pathway for the Dehydrogenation of *N*-Heterocycles**



Indeed, the oxidation of **1a** succeeded even at lower temperature (80 °C) with desired product formed in 78% yield if  $\text{H}_2\text{O}_2$  is used as the oxidant instead of air. As shown in Table 3, the catalytic dehydrogenation of 1,2,3,4-tetrahydroquinoxaline

occurred and the product quinoxaline (**4d**) was generated in quantitative yield suggesting that the oxidation sequence commences with the formation of the corresponding imine ( $\text{C}=\text{N}$ ). The final product is obtained by another dehydrogenation reaction, which probably takes place after tautomerization as investigated by Jones and co-workers.<sup>11c</sup>

**Scheme 3, Control Experiments**



In agreement with this proposal no dehydrogenation product was detected when using 2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline (**9a**) as substrate (Scheme 3). Furthermore, the dehydrogenation of 1-(indolin-1-yl)ethan-1-one (**9b**) was also not observed, which suggests that the direct formation of a  $\text{C}=\text{C}$  is difficult. This result also demonstrates that the presence of the  $\text{N-H}$  motif in the cycloalkane is critical for the dehydrogenation, which might be favorable for the adsorption of the starting material onto the catalyst surface.

## CONCLUSION

In summary, we demonstrated for the first time that nanostructured iron oxides surrounded by nitrogen-doped-graphene shells immobilized on carbon support (labelled  $\text{FeO}_x\text{@NGr-C}$ ) constitute an active catalyst for the dehydrogenation of *N*-heterocycles. The catalytic material is easily obtained in a practical and scalable two-step method via pyrolysis of simple iron acetate and phenanthroline and subsequent selective leaching. The optimized material allows for green dehydrogenations of several *N*-heterocycles. The utility of the methodology is also shown by the synthesis of pharmaceutically relevant quinolines.

## ASSOCIATED CONTENT

### Supporting Information

Extended data about optimization of reaction conditions; preparation, characterization and recovery of  $\text{FeO}_x\text{@NGr-C}$ ; mechanism investigations and synthesis and spectroscopic data of products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interests.

## ACKNOWLEDGMENT

This work was supported by the state of Mecklenburg Vorpommern and F. Hoffmann-La Roche. We thank Dr. Carsten Kreyenschulte, Dr. Jabor Rabeah and Dr. Jörg Radnik for technical assistance.

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