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# A reusable CNTs-supported single-atom iron catalyst for the highly efficient synthesis of C-N bonds

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Abstract: C-N bond formation is regarded as a very useful and fundamental reaction, which is important for the synthesis of nitrogen-containing molecules in both organic and pharmaceutical chemistry. Noble metal and homogeneous catalysts have been used for C-N bond formation frequently, however, there are still some problems for these catalysts such as high cost, serious pollution and low atom economy. Herein the low-toxic and cheaper iron complex was loaded on CNTs and the heterogenous single-atom catalyst (SAC) named Fe-N<sub>x</sub>/CNTs was prepared. We applied this SAC to the synthesis of C-N bonds for the first time. It was found that Fe-N<sub>x</sub>/CNTs was an efficient catalyst for the synthesis of C-N bonds from aromatic amines and ketones. The catalytic performance is markedly excellent with the yield up to 96%, 6-fold higher than that of noble metal catalysts such as AuCl<sub>3</sub>/CNTs and RhCl<sub>3</sub>/CNTs. It was suitable for up to 13 aromatic amine substrates with no additives and 17 enaminones were obtained. By using high-angle annular darkfield scanning transmission electron microscopy (HAADF-STEM) in combination with X-ray adsorption spectroscopy (XAS), we have observed iron species of Fe-N<sub>x</sub>/CNTs were in good dispersion as single atoms and Fe-Nx might be the catalytic active site. This Fe-N<sub>x</sub>/CNTs catalyst has potential industrial application for its seven runs without any significant loss of activity.

## Introduction

Carbon nanotubes (CNTs), with thin planar sheet of sp<sup>2</sup>-bonded carbon atoms densely packed in a honeycomb crystal lattice, was first reported by Lijima in 1991.<sup>[1]</sup> Due to the high surface area and excellent electronic conductivity,<sup>[2-6]</sup> CNTs are good supports for metals to promote some chemical reactions. Several reports in the literature have shown that CNTs-supported

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transition metals exhibited a much-enhanced activity in the oxygen reduction reactions (ORR).<sup>[7-14]</sup> In addition, some CNTs-supported metals like Pd, Ru, Pt and Ni can be used for hydrogen production from hydrogen iodide and ammonia decomposition.<sup>[15-20]</sup> Apart from these many inorganic reactions, some organic reactions involving the application of CNTs were also reported.<sup>[21-24]</sup> For instance, Kobayashi and coworkers<sup>[24]</sup> developed a nickel-based Lewis acid integrated with CNTs for the asymmetric synthesis of nitrones in water. So we envisioned that more non-noble-metals-CNTs could be prepared to efficiently synthesize some important compounds in organic chemistry or pharmaceutical chemistry.

Single-atom catalysts (SACs) are a type of atomically dispersed catalysts with mono-nuclear metal complexes or single metal atoms anchored on supports. Due to the metal single atoms are easy to anchor to substrates and form strong interactions with the support,[25] the SACs have demonstrated superior catalytic performances, such as high activity and selectivity. Since Zhang firstly reported about the application of SACs on the CO oxidation in 2011,<sup>[26]</sup> various types of metal SACs have been successfully designed and used in the field of fuel processing, chemicals production and environmental remediation etc.<sup>[27-32]</sup> To date, several literature report that single atom Fe-N<sub>x</sub> materials exhibit promising catalytic performances in a variety of reactions.<sup>[33-36]</sup> Fe-N<sub>x</sub> materials would discard the noble-metal usage and perform high utilization potential for industry. Taking into consideration the excellent activity of SACs as well as the excellent adsorption property of carbon materials, anchoring single atom Fe-N<sub>x</sub> materials on CNTs is thus expected to be effective to improve the catalyst performance in organic synthesis.

The nitrogen-containing molecules is very prevalent in pharmaceutical agents, natural products, functional materials and synthetic intermediates. The key to the synthesis of nitrogen-containing molecules is the formation of C-N bonds.<sup>[37]</sup> Many strategies have been continuously developed to achieve efficient synthesis of C-N bonds. However, these strategies involve many noble metal catalysts and non-recyclable homogeneous catalysts<sup>[38-42]</sup> which increase the cost of catalysts and violate the concept of green chemistry and atom economy. So cheap and easily recyclable heterogeneous catalysts are attracting much more attention.

In this study we report a reusable and heterogeneous SAC named Fe-N<sub>x</sub>/CNTs, which shows high activity to promote the synthesis of  $\beta$ -enaminones by the efficient construction of C-N bonds. Notably, this is the first time that the SAC has been applied to the C-N bonds construction. The catalytic performance of Fe-N<sub>x</sub>/CNTs is markedly better than that of noble metal catalysts such as AuCl<sub>3</sub>/CNTs and RhCl<sub>3</sub>/CNTs, with the yield up to 96%, 6-fold higher than that of AuCl<sub>3</sub>/CNTs and RhCl<sub>3</sub>/CNTs. More importantly, by using high-angle annular darkfield scanning

transmission electron microscopy (HAADF-STEM) in combination with X-ray adsorption spectroscopy (XAS), we observe that iron species of Fe-N<sub>x</sub>/CNTs are in good dispersion as single atoms and Fe-N<sub>x</sub> might be the catalytic active site.

## **Results and Discussion**

The iron complex was prepared according to the reported literature (see the Experimental Section for more details).<sup>[43-45]</sup> To demonstrate that the iron complex was formed successfully, fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) were used. As shown in Fig. S1, the FTIR spectrum showed four characteristic peaks (2974, 2910, 1601, 1085 cm<sup>-1</sup>), which were identical with those reported previously.<sup>[43]</sup> Also, the XRD peaks of iron complex (Fig. S2) match well with the simulated one (JCPDS 51-2309). Then the obtained iron complex was supported on CNTs to form Fe-N<sub>x</sub>/CNTs. The Fe and N mass contents of Fe-N<sub>x</sub>/CNTs were 3.3% and 3.7% respectively through the test of X ray fluorescence (XRF), indicating that the iron loading of Fe-N<sub>x</sub>/CNTs was low and the molar ratio of Fe:N was about 1:4. Brunauer-Emmett-Teller (BET) measurement has been performed to analyze specific surface area and pore diameter of related catalysts. N2 isotherms as shown in Figure S3 were close to Type IV curve and the surface area of the catalysts was shown in Table S1. Fe-N<sub>x</sub>/CNTs exhibited the smaller surface area (171 m<sup>2</sup>·g<sup>-1</sup>) and total pore volume (0.267 cm<sup>3</sup>·g<sup>-1</sup>) than the CNTs which resulted from the loading of iron complex.

The morphology and microstructure of the prepared catalyst Fe-N<sub>x</sub>/CNTs were investigated by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) measurements. As shown in the Fig. 1a, no-load CNTs exhibited a smooth and tubular structure. After iron complex was supported on CNTs, the surface of CNTs became rough (Fig. 1b). However, we didn't detect any obvious metallic Fe species from HRTEM images (Fig. 1d), suggesting that the size of Fe species may be reduced to below the resolution of HRTEM with iron element in good dispersion. In addition, from the XRD pattern of Fe-N<sub>x</sub>/CNTs (Fig. S4), amorphous and graphitic carbon characteristic peaks were observed without distinct Fe<sub>3</sub>C and metallic Fe peaks. This consistently indicated that the Fe species were dispersed well in the CNTs.<sup>[46,47]</sup> To our delight, the HAADF-STEM images showed individual Fe atoms were well dispersed in the CNTs (Fig. 1e and 1f), indicating that the Fe-N<sub>x</sub>/CNTs was a kind of SACs.

For comparison, the catalyst FeSO<sub>4</sub>/CNTs which showed low catalytic activity (Table 2, entry 7) was prepared through similar conditions. Elemental analysis of the catalysts were then carried out by X-ray photoelectron spectroscopic (XPS) measurements. As revealed in Fig. S5a, the survey of Fe-N<sub>x</sub>/CNTs demonstrated the presence of C, N, O and Fe elements, while the survey of FeSO<sub>4</sub>/CNTs confirms the presence of C, O, S and Fe. The presence of the oxygen was the result of oxidation of carbon materials when handled under catalyst preparation conditions.<sup>[48]</sup> The deconvolution of the N 1s spectrum for Fe-N<sub>x</sub>/CNTs (Fig. 2a) showed the presence of two types of nitrogen species, which could be attributed to C-N (at around 401.1 eV)<sup>[49,50]</sup> and Fe-N<sub>x</sub> ( at around 399.8 eV) species.<sup>[51-53]</sup> The presence of two types of nitrogen species were obviously due to the loading of the iron complex. Moreover, the XPS Fe<sup>2+</sup> and Fe<sup>3+</sup> peaks of Fe-N<sub>x</sub>/CNTs

were presented in Fig. 2b. The peaks at 710.5 eV and 724.5 eV were assigned to Fe<sup>2+</sup> and the peaks at 712.3 eV and 727.0 eV were assigned to Fe<sup>3+</sup>. This indicated that different coordinated Fe-N<sub>x</sub> species co-existed in the sample, and some Fe oxides may also be included due to the hydrothermal preparation process. In addition, the deconvolution of Fe 2p spectrum (Fig. S5b) for FeSO<sub>4</sub>/CNTs also showed the presence of Fe<sup>2+</sup> and Fe<sup>3+</sup> species, which could be attributed to Fe-O<sub>x</sub> species (maybe Fe oxides or FeSO<sub>4</sub>). Therefore, the distinct difference between Fe-N<sub>x</sub>/CNTs and FeSO<sub>4</sub>/CNTs was about Fe coordination environment, and Fe-N<sub>x</sub> exhibited higher activity than Fe-O<sub>x</sub> as shown in Table 2, entries 1 and 7. Considering that only on the catalyst surface the iron species can be detected by XPS,<sup>[54]</sup> more specific chemical environment of Fe in our catalyst need to be explored.



Figure 1. (a) SEM image of CNTs. (b) SEM image of Fe-N<sub>x</sub>/CNTs. (c) TEM image of CNTs. (d) TEM image of Fe-N<sub>x</sub>/CNTs. (e) HAADF-STEM image showing individual Fe atoms of Fe-N<sub>x</sub>/CNTs. (f) Enlargement of image (e).



Figure 2. (a) High-resolution spectra of N 1s for Fe-N<sub>x</sub>/CNTs. (b) High-resolution spectra of Fe 2p for Fe-N<sub>x</sub>/CNTs.

XAS is a unique tool for studying the local structure around a selected element even with low element content. Herein, the Fe-N<sub>x</sub>/CNTs and FeSO<sub>4</sub>/CNTs were further characterized by XAS for obtaining the oxidation state, structural and coordination

environment of Fe-absorbing atom. The k<sup>3</sup>-weighted extended X-ray absorption fine structure (EXAFS) spectra at the Fe K-edge for our catalysts were measured and the corresponding fourier transform spectra in R space were shown in Fig. 3a and 3b. From the data fitting results in Table 1, we found the FeSO<sub>4</sub>/CNTs, which had low catalytic activity in the synthesis of C-N bonds (Table 2, entry 7) showed a distinct Fe-O coordination with a coordination number of 1.9. This result suggested that the Fe-O<sub>x</sub> structure could be attributed to FeSO<sub>4</sub> and may include small amount of Fe<sub>2</sub>O<sub>3</sub>. For the Fe-N<sub>x</sub>/CNTs catalyst, a primary peak was found at about 1.5 Å which corresponded to the Fe-N scattering path with a coordination number of 4 suggesting that most of Fe species were well dispersed in the Fe-Nx/CNTs and were four-fold coordinated by N atoms. Considering that Fe<sup>2+</sup> and Fe<sup>3+</sup> species co-existed according to the XPS analysis, the Fe-N<sub>x</sub> structure could be assigned to Fe<sup>2+</sup>-N<sub>4</sub> and Fe<sup>3+</sup>-N<sub>4</sub>.<sup>[47]</sup> In addition, Fe-O coordination also existed with a coordination number of 3. revealing the presence of Fe oxides (may be Fe<sub>2</sub>O<sub>3</sub>). But the content of Fe-Ox species was relatively low (~6%) from the EXAFS data fitting results, so Fe-N<sub>x</sub> species could be the real active site in Fe-N<sub>x</sub>/CNTs.

Fig. 3c shows the normalized X-ray absorption near-edge structure (XANES) spectra at the Fe K-edge of the Fe Foil, FeSO<sub>4</sub>/CNTs and Fe-N<sub>x</sub>/CNTs. White-line intensity can reflect the oxidation state of the Fe species. We found the white-line intensity of FeSO<sub>4</sub>/CNTs was strongest, indicating most Fe species were oxidized. This is consistent with the formation of Fe-O coordination from FeSO<sub>4</sub>/CNTs EXAFS fitting results. Moreover, the white-line intensity of Fe-N<sub>x</sub>/CNTs was higher than that of Fe foil, suggesting that the Fe species in Fe-N<sub>x</sub>/CNTs became more positively charged and were coordinated with some elements. Meanwhile, the pre-edge peak at about 7115 eV for Fe-N<sub>x</sub>/CNTs, which was different from those of FeSO<sub>4</sub>/CNTs and Fe foil in position, shape and intensity, can be assigned to Fe 1s $\rightarrow$ 3d transition, a quadruple allowed transition, and it was considered as a possible fingerprint of the  $\text{Fe-N}_{\text{x}}$  structure.<sup>[55]</sup> This is consistent with the analysis about Fe-N<sub>4</sub> coordination formation of EXAFS.



**Figure 3.** Fourier-transformed K-edge EXAFS of Fe for (a) FeSO<sub>4</sub>/CNTs and (b) Fe-N<sub>x</sub>/CNTs. The data ranges used for data fitting in R space ( $\Delta$ R) are 1.0-2.0 Å. (c) Normalized XANES spectra at Fe K-edge of Fe foil, FeSO<sub>4</sub>/CNTs and Fe-N<sub>x</sub>/CNTs.

In order to investigate the application of this type of catalyst for synthesis of C-N bonds. 1-Phenylbutane-1,3-dione (1a) and aniline (2a) were taken as model substrates to synthesize  $\beta$ -enaminones through the construction of C-N bonds. To our

delight, in the presence of Fe-Nx/CNTs, at 110 °C in toluene under air, the desired product (Z)-1-phenyl-3-(phenylamino) but-2-en-1-one (3a) was obtained in 94% GC yield (Table 2, entry 1). Further experiments indicated that catalysts were important in this aromatic amines involved condensation reaction, as none of the desired product was detected in the absence of catalyst or only using CNTs (Table 2, entry 2-3). This result prompted us to explore other catalysts. The yields of 3a decreased to 13% and 15% when noble metal catalysts AuCl<sub>3</sub>/CNTs and RhCl<sub>3</sub>/CNTs were used (Table 2, entries 4-5), indicating the high efficiency of Fe-N<sub>x</sub>/CNTs. Notably, using iron complex as the catalyst obviously reduced the reaction efficiency (Table 2, entry 6). This could be due to the fact that the iron complex was difficult to coordinate with other elements for its saturated six-fold coordinated structure, however, the initiation of this reaction required the coordination of metals with the carbonyl oxygen of the substrate 1 (Fig. 8).[56] In addition, due to the absence of active site Fe-Nx species, FeSO4/CNTs could provide the product, but in an unsatisfactory yield (Table 2, entry 7). The vield of 3a improved to 96% when the amount of Fe-N<sub>x</sub>/CNTs was lowered to 150 mg. But the yield of 3a reduced to 91%, using a smaller loading of Fe-N<sub>x</sub>/CNTs (Table 2, entries 8-9). The effect of solvents (1,4-dioxane, DMF, EtOH and DCE) were then examined and found that DCE could improve the yields (96% GC yield and 88% isolated yield, Table 3, entries 10-13). Lowering the reaction temperature to 70 or 60 °C deteriorated the yield (Table 2, entries 14-15). Thus, it was concluded that the optimized reaction conditions were achieved with Fe-Nx/CNTs (150 mg) as the catalyst in DCE at 80 °C (Table 2, entry 13). In addition, the TON values of related catalysts were also shown in the Table S2. It was obvious that the catalytic activity of Fe-N<sub>x</sub>/CNTs was highest.

Table 1. EXAFS Data Fitting Results at Fe K-Edge for the Fe Foil, FeSO<sub>4</sub>/CNTs, and Fe-N<sub>2</sub>/CNTs Catalysts.

Samples	Shell	CNª	R (Å) <sup>b</sup>	$\sigma^2$ (10 <sup>2</sup> Å <sup>2</sup> ) <sup>c</sup>	R factor
FeSO <sub>4</sub> /CNTs	Fe-O	1.9	2.16	0.94	0.0097
Fe-N <sub>x</sub> /CNTs	Fe-N	4.0	2.08	0.09	0.0089
	Fe-O	3.0	1.98	0.19	

[a] Coordination number for the absorber-backscatterer pair. [b] Average absorber-backscatterer distance. [c] Debye-Waller factor. The accuracies of the above parameters were estimated as follows: CN, ±20%; R, ±1%;  $\sigma^2$ , ±20%.

With these optimized reaction conditions in hand, we further aimed to apply the catalyst Fe-N<sub>x</sub>/CNTs to synthesize diverse  $\beta$ -enaminones for their significance in organic synthesis.<sup>[57-63]</sup> As summarized in Scheme 1, the reaction went smoothly between various aromatic amines with the substrates 1 and afforded the corresponding  $\beta$ -enaminones products in moderate to good isolated yields. It's worth mentioning that all scope reactions were performed on 2 mmol scale. Aromatic amines 2 with electron-donating substituents on the aromatic ring, such as methyl or methoxy, were well tolerated for this process (**3b-e**, 85-90%). Electron-withdrawing substituents 4-fluoro, 4-chloro, 4-bromo, 4-trifluoromethyl groups lessened the yields of the desired products **3f-g** (73-75%), **3j-k** (56-79%). These results showed an obvious electronic effect. 4-Cl, 3-Cl, 2-Cl groups on

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the aryl group of substrates **2** prove a positive steric effect on the yield of **3g** (75%), **3h** (54%) and **3i** (50%), respectively. To our delight, naphthylamine **2l** underwent this reaction as well and the desired product **3l** was obtained in good yield (78%), without exhibiting steric hindrance. However, the target product **3m** was formed in a relatively low yield (47%) owing to the increased steric hindrance of substrates **1b** ( $R^2 = Ph$ ). The substrates pentane-2,4-dione (**1c**) and ethyl 3-oxobutanoate (**1d**) revealed good reactivity to obtain efficiently the target products **3n-o** (80-89%).

**Table 2.** Optimization of Reaction Conditions<sup>a</sup>.

		NH <sub>2</sub> <u>cat.</u> solvent,		
Ť	1a	2a	3	a
Entry	Catalyst <sup>b</sup>	Solvent	Temp. (°C)	Yield <sup>c</sup> (%)
1	Fe-N <sub>x</sub> /CNTs	toluene	110	94
2	-	toluene	110	trace
3	CNTs	toluene	110	trace
4	AuCl <sub>3</sub> /CNTs	toluene	110	13
5	RhCl <sub>3</sub> /CNTs	toluene	110	15
6	Iron complex	toluene	110	16
7	FeSO <sub>4</sub> /CNTs	toluene	110	45
8	Fe-N <sub>x</sub> /CNTs <sup>d</sup>	toluene	110	96
9	Fe-N <sub>x</sub> /CNTs <sup>e</sup>	toluene	110	91
10	Fe-N <sub>x</sub> /CNTs <sup>d</sup>	1,4-dioxa ne	100	95
11	Fe-N <sub>x</sub> /CNTs <sup>d</sup>	DMF	110	86
12	Fe-N <sub>x</sub> /CNTs <sup>d</sup>	EtOH	80	86
13	Fe-N <sub>x</sub> /CNTs <sup>d</sup>	DCE	80	96(88 <sup>f</sup> )
14	Fe-N <sub>x</sub> /CNTs <sup>d</sup>	DCE	70	95
15	Fe-N <sub>x</sub> /CNTs <sup>d</sup>	DCE	60	90

[a] Conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), catalyst (200 mg), solvent (5 mL), air, 13 h. [b] The metal contents are equimolar with Fe-N<sub>x</sub>/CNTs. [c] GC yield with mesitylene as the internal standard. [d] 150 mg. [e] 100 mg. [f] Isolated yield given in parentheses.

The substrate scope reactions were carried out on 2 mmol scale, and encouraged by their success, Fe-N<sub>x</sub>/CNTs was used in a larger scale preparative reaction to demonstrate its practical utility. The condensation of 1-phenylbutane-1,3-dione (8 mmol) and *p*-toluidine (16 mmol) was carried out on 1.30 gram scale to give target product (**3b**) in 83% isolated yield (eq 1, Scheme 2). To further demonstrate the value of this catalyst, the Fe-N<sub>x</sub>/CNTs catalyst system was used for the synthesis of some pharmacologically active compounds. As shown in the Scheme 2, the condensation reactions proceed smoothly to give corresponding products **DM27** and H<sub>2</sub>L<sup>4</sup> in good yields (eq 2-3). **DM27** is a P-gp efflux inhibitor which can enhance the oral bioavailability of antiviral drugs<sup>[64]</sup> and H<sub>2</sub>L<sup>4</sup> is a non-cytotoxic compound with antibacterial activity.<sup>[65]</sup>

To demonstrate that the  $\beta$ -enaminones are a kind of very versatile key intermediates in organic synthesis, as shown in Scheme 3, compounds **3a** and **3b** were treated with tosyl azide by employing *t*-BuOK as the base promoter to give the 1,2,3-triazole **4a** and **4b** in good yields which could be used in chemical biology and medicinal chemistry.<sup>[66,67]</sup> Moreover,  $\beta$ -enaminones could be cyclized to form the isoxazoles under the

acid atmosphere,<sup>[68]</sup> so trifluoroacetic acid was used as the strong acid to promote the cyclization and the isoxazoles **5a** and **5b** were obtained in excellent yields. Furthermore, the internal olefin of  $\beta$ -enaminones could be chlorination by N-chlorosuccinimide (NCS) to give the products **6a** and **6b** in excellent yields.<sup>[69]</sup>



Scheme 1. Substrate Scope for the synthesis of  $\beta$ -enaminones. Reaction conditions: 1 (2 mmol), 2 (4 mmol), Fe-N<sub>x</sub>/CNTs (600 mg), DCE (20 mL), 80 °C, 24 h, 0.1 MPa air. Isolated yields are given.

**30**, 80%

**3n**, 89%





3m, 47%



Scheme 3. Functionalization of  $\beta$ -enaminones.

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The recycling of the catalyst is very important for industrial applications. After filtration and washing with DCE, we could reuse the Fe-N<sub>x</sub>/CNTs for the condensation of 1-phenylbutane-1,3-dione (1a) with aniline (2a) or 4-methoxyaniline (2e). The results were shown in Fig. 4. The condensation reaction was carried out six times under identical reaction conditions with the recycling of Fe-N<sub>x</sub>/CNTs. The yields of the products were 85% and 75% respectively when using fresh Fe-N<sub>x</sub>/CNTs. No significant decrease was observed in the next six runs and the sixth yields of the product were 82% and 72% respectively. So the catalyst Fe-N<sub>x</sub>/CNTs showed a good reactivity up to 6 cycles without any significant loss of activity or yield of the desired products.



Figure 4. Catalyst Reusability. 1-phenylbutane-1,3-dione (2 mmol), aniline or 4-methoxyaniline (4 mmol) and catalyst Fe-N<sub>x</sub>/CNTs (600 mg) at 80 °C in DCE.

### Conclusion

In summary, a SAC Fe-N<sub>x</sub>/CNTs was prepared by a simple method for the highly efficient synthesis of C-N bonds. The catalytic performance of Fe-N<sub>x</sub>/CNTs is superior to noble metal catalysts like AuCl<sub>3</sub>/CNTs and RhCl<sub>3</sub>/CNTs. Such outstanding performance originates from the introduction of SAC and electronic coupling between iron species and CNTs. By using HAADF-STEM in combination with XAS, we have observed iron species of Fe-N<sub>x</sub>/CNTs were in good dispersion as single atoms and Fe-N<sub>x</sub> might be the catalytic active site. In addition, the Fe-N<sub>x</sub>/CNTs catalyst system can be run on a gram-scale and the product β-enaminones can be functionalized to form some important nitrogen-containing compounds. Furthermore, the Fe-N<sub>x</sub>/CNTs has stable catalytic activity, evidenced by the reusability of the catalyst for seven runs with minimal loss in activity. This work should shed light on the design of more effective metal-CNTs SAC to be applied in organic synthesis.

## **Experimental Section**

**Preparation of Fe-N<sub>x</sub>/CNTs.** A mixture of FeCl<sub>3</sub>·6H<sub>2</sub>O (3 mmol) and ethylenediamine (EDA, 6 mmol) in EtOH (30 mL) was stirred at 80 °C for 2 h. After cooling to ambient temperature, the brown precipitate was filtered, washed with EtOH three times, and dried under 60 °C for 4 h to afford the six-fold coordinated iron complex (Fe-EDA). Then, 220 mg of Fe-EDA and 1 g of CNTs were stirred in EtOH (30 mL) for 2 h. The as-obtained suspension liquid was kept in the sealed hydrothermal synthesis reactor at 120 °C for 27 h, then the temperature was lowered to 60 °C for 14 h.

Finally, the suspension liquid was transfered to the muffle furnace at 180  $^{\rm o}C$  for 1 h to give the catalyst Fe-Nx/CNTs as black powder.

Preparation of AuCl<sub>3</sub>/CNTs, RhCl<sub>3</sub>/CNTs and FeSO<sub>4</sub>/CNTs. 270 mg AuCl<sub>3</sub> (0.89 mmol), 202 mg (0.89 mmol) RhCl<sub>3</sub>·H<sub>2</sub>O or 248 mg (0.89 mmol) FeSO<sub>4</sub>·7H<sub>2</sub>O and 1 g of CNTs were stirred in EtOH (30 mL) for 2 h. The next loading process was the same as Fe-N<sub>4</sub>/CNTs. Notably, the metal contents of these catalysts were equimolar with Fe-N<sub>4</sub>/CNTs for catalytic activity comparison.

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A reusable single atom catalyst Fe-N<sub>x</sub>/CNTs is prepared and can be applied to the synthesis of C-N bonds. The catalytic performance of Fe-N<sub>x</sub>/CNTs is superior to noble metal catalysts like AuCl<sub>3</sub>/CNTs and RhCl<sub>3</sub>/CNTs. Such outstanding performance originates from the introduction of SAC and electronic coupling between iron species and CNTs.



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