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# Atomically Dispersed Zn-N<sub>x</sub> Sites in N-Doped Carbon for Reductive N-formylation of Nitroarenes with Formic Acid

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#### Dedication ((optional))

**Abstract:** Replacement of noble metal catalysts with low-cost, nonnoble heterogeneous catalysts is highly desirable. Herein, we prepared a reactive, inexpensive and stable isolated single-atom Zn/N-doped porous carbon (ZnNC) catalyst derived from a versatile zeolitic imidazolate framework precursor. The optimized ZnNC-1000 with Zn-N<sub>x</sub> species possesses high zinc loading (5.2 wt%) and nitrogen content (6.73%), exhibits efficient catalytic performance in the one-pot N-formylation of nitroarene to the corresponding formamides by using formic acid as the hydrogen donor and formylation agent.  $H_2$ -D<sub>2</sub> exchange reaction and HCOOHchemisorption experiments demonstrated that atomically dispersed Zn-N<sub>x</sub> species are essential for the activation of hydrogen and HCOOH molecules, which finally contributed to the highest catalytic activity of ZnNC-1000 for the reductive N-formylation reaction.

Catalytic hydrogenation is a fundamental process in the fine chemical industry.<sup>[1]</sup> The most of traditional heterogeneous hydrogenation catalysts are based on expensive and rare transition noble metals, such as Pd, Au, Ru, Pt, etc. However, high cost and scarcity of these metals require the development of efficient alternative earth-abundant non-noble metal-based catalysts. In recent years, N-doped carbon supported metal catalysts (such as Fe, Co and Ni, etc.) have attractive considerable attention in hydrogenation reaction due to their excellent activity and chemoselectivity.<sup>[2]</sup> These materials usually prepared by the carbonization of metal-organic-frameworks (MOFs) or organometallic complex.<sup>[3]</sup> There is a general agreement that both metallic species and nitrogen of the catalysts play an important role in enhancing the catalytic performance. While, the active sites for the hydrogenation reaction are still controversial due to the heterogeneity of the metallic species (accessible and inaccessible nanoparticles encapsulated by graphite shells, single atoms coordinated with nitrogen  $(M-N_x)$ , etc), which will greatly hinder the development of highly active and durable catalysts.

Formic acid (FA) with considerable hydrogen content (4.4 wt %), is an excellent alternative to  $H_2$ .<sup>[4]</sup> More importantly, FA can be easily obtained from biomass in high yields.<sup>[5]</sup> Therefore, FA is an

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economical and easy-to-handle liquid hydrogen donor. In addition, formic acid and its derivatives can also be used as the formylating reagents in the N-formylation of anilines.<sup>[6]</sup> Some of these processes could proceeded under mild reaction conditions. To date, however, only fewer non-noble (Fe, Co and Ni) metal catalysts have been used in the reductive N-formylation reaction of nitroarenes by using FA or formate as the hydrogen source and formylation reagents.<sup>[7]</sup> On the other hand, although the catalytic reductive N-formylation of anilines over transition metal oxide by using CO<sub>2</sub> as a carbonyl source has been well demonstrated,<sup>[8]</sup> these processes usually require noble metals under harsh reaction conditions. Moreover, the aryl amines used as starting materials are usually prepared by the reduction of nitroarenes over transition metals under a high pressure of hydrogen. Therefore, it is highly desirable to develop an alternative base metal catalyst for the reductive N-formylation reaction directly from readily available nitroarenes.

Zinc is a promising material owing to the abundant reserves and non-toxic character. However, zinc was usually used as the modifier to improve the selectivity or combined with other transition metals served as the efficient hydrogenation catalyst and zinc oxide alone was only active for the hydrogenation of C=C/C=C bonds.<sup>[9]</sup> Herein, we report an atomically dispersed zinc catalyst (ZnNC) with Zn-Nx active sites derived from zeolitic imidazolate framework precursor (ZIF-8) for the reductive Nformylation of nitroarenes to formamides by using FA as the hydrogen source and formylation agent. The optimal catalyst ZnNC-1000 displayed efficient catalytic performance, good stability and well substrate scope in the reductive N-formylation of nitroarenes to formamides. For comparison, the controlled samples ZnO, Zn@C and N-C were almost inactive for the reductive N-formylation of nitroarenes. In addition, H<sub>2</sub>-D<sub>2</sub> exchange reaction and HCOOH chemisorption experiments demonstrated that atomically dispersed zinc and uniform nitrogen sites contribute significant role to the efficient catalytic performance.

The ZnNC samples were prepared by directly pyrolyzed the synthesized ZIF-8 nanoparticles at desired temperatures (Figure S1 and S2). Then the obtained samples were denoted as ZnNC-T (T=800, 900, 1000 and 1100 °C). The morphologies and microstructures of ZnNC-T samples were first characterized by transmission electron microscopy (TEM). The ZnNC-T (-800, 900, and 1000) samples exhibited a three-dimensional (3D) cellular structure (Figure 1a and S3), which was totally different from the ZIF-8 precursor with dodecahedral structure. While the ZnNC-1100 displayed nonporous structure due to the evaporation of Zn at high thermal annealing temperature (Figure S4).<sup>[10]</sup> The absence of Zn particles in the high-resolution TEM (HRTEM) image indicated the Zn was atomically dispersed single zinc atoms were further identified by isolated bright dots detected by

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the aberration-corrected high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) (Figure 1c). In addition, the elemental mappings and energy dispersive X-ray spectrometer (EDS) indicated that C, N and Zn elements were uniformly distributed throughout the entire framework. (Figure 1d and Figure S5).



Figure 1. a) TEM, b) HRTEM, c) The aberration-corrected HAADF-STEM images and enlarged images, d) corresponding elemental mappings showing the uniformly distribution of C, N and Zn, of ZnNC-1000.

The N<sub>2</sub> adsorption-desorption isotherms of ZnNC-800, -900 and -1000 are type IV isotherm indicate the presence of meso-pores and micropores, which might originate from the inheritance of porous ZIF-8 precursor (Figure S2d and S6).<sup>[11]</sup> The surface area was increased from 659 to 952 m<sup>2</sup>/g and then decreased to 121 m<sup>2</sup>/g when the pyrolysis temperature increased from 800 to 1100 °C (Table S1), suggesting the pyrolysis temperature played an important role in the formation of the catalyst structure (details explanations see Figure S7). XRD results showed that all ZnNC-T samples have similar spectra featuring the characteristic peaks of amorphous carbon with 20 at ~26° and 43°, respectively (Figure S8). While no diffraction peaks corresponding to Zn or ZnO species were observed, excluding the presence of large crystalline particles of zinc species. The Raman spectra of ZnNC-T samples with different pyrolysis temperature (Figure S9) showed two peaks at Raman shift ~1350 and 1580 cm<sup>-1</sup>, indicating the D band and G band in graphite, respectively. The intensity ratio of D to G bands (ID/IG) followed an order of ZnNC-800 (1.22) > ZnNC-900 (1.08) > ZnNC-1000 (1.05) > ZnNC-1100 (0.99), suggesting an upward trend of the graphitization degree with the increase of the pyrolysis temperature.

The Zn and N content of the ZnNC-T samples were determinate by inductively coupled plasma optical emission spectrometry (ICP-OES) and elemental analyses respectively. The Zn and N content decreased from 19.2 wt% to 2.1 wt% and 17.84 wt% to 4.01 wt% respectively when the pyrolysis temperature increased from 800 to 1100 °C (Figure S4). To further investigate surface composition of ZnNC-T samples, high resolution X-ray photoelectron spectroscopy (XPS) was performed. The surface Zn content decreased from 5.48 atom% (ZnNC-800) to 1.43 atom% (ZnNC-1000) and only 0.56 atom% was retained in ZnNC-1100 (Table S3). The N 1s XPS spectra exhibited four peaks with binding energies of 398.5, 399.6, 400.2, and 401.2 eV, corresponding to pyridinic N, Zn-N<sub>x</sub>, pyrrolic N, and graphitic N, respectively (Figure 2a-d).<sup>[12]</sup> The relative content of pyridinic N in ZnNC-800 and ZnNC-900 was 37.4% and 38.2%, and then decreased to 30.5% and 26.4% for ZnNC-1000 and ZnNC-1100 (Figure S10). All these samples possessed the Zn-N<sub>x</sub> species, and the relative content Zn-Nx was decreased in the following order ZnNC-800 (26.2%) > ZnNC-1000 (23.1%) > ZnNC-900 (21.7%) > ZnNC-1100 (21.4%) (Figure 2). While, pyrrolic-N and graphitic-N content increased gradually with the increase of pyrolysis temperature, which might be due to some of the resultant pyridinic-N and Zn-N<sub>x</sub> transformed to graphitic N.



Figure 2. High resolution N 1s spectra of ZnNC-800, -900, -1000 and -1100.

Initially, the hydrogenation performance of ZnNC-T samples was evaluated in the reductive N-formylation of nitrobenzene by using FA as the hydrogen source and formylation agent. Among all prepared ZnNC-T samples, ZnNC-1000 showed the best performance with 42% conversion and 99% selectivity (entries 1-4). This demonstrated that the pyrolysis temperature played a significant role on the catalytic performances. To verify the role of Zn and nitrogen, Zn@C and N-C without nitrogen or zinc precursor was prepared under the same conditions as that of ZnNC-1000 respectively. However, poor catalytic performance was observed when they were used as catalysts (entries 5 and 6), indicating that both N and Zn played an important role in the activation of FA. Moreover, ZIF-8 and Zn(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O also showed lower activity in the reductive Nformylation reaction (entries 7 and 8). Although ZnO was able to hydrogenate unsaturated C=C or C≡C bonds by using H<sub>2</sub>,<sup>[9c,</sup> <sup>13]</sup> it has never been used in the reductive reaction using FA as the hydrogen source. Herein, ZnO was used as the catalyst for the reductive N-formylation reaction. However, ZnO displayed poor activity in the present reductive N-formylation reaction

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(entry 9), implying that ZnO could not be the active species for the reaction. Therefore, we performed control experiments to further exploration the exact role of ZnNC-1000 in the reaction. It is obviously that no reaction was proceed without a catalyst (entry 10), indicating the catalyst was necessary for the reaction. While 91% of aniline were convert into Nphenylformamide (entry 11), implying the formylation of aniline was an uncatalyzed process. This is different with the previous literatures that solvent control the selectivity when formic acid was used as the hydrogen and formylating source.<sup>[14]</sup> And 36% conversion of 1a with 84% selectivity of 2a were obtained even when 3 equivalent FA were used in the N-formylation reaction (entry 12). Therefore, ZnNC-1000 catalyst played an important role for the reduction of nitrobenzene.

Table 1. Zn-catalytic one-pot reductio	n N-formylation of nitrobenzene <sup>[a</sup>	]
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N	0 <sub>2</sub>	catalyst	, A A A A A A A A A A A A A A A A A A A	2
	FA,	150 °C, 2 mL THF		

	14			28		
Entry <sup>[a]</sup>	catalyst	t(h)	FA	Con.	Sel.	TON
1	ZnNC-800	5	12	8.2	47	0.7
2	ZnNC-900	5	12	31	88	3.8
3	ZnNC-1000	5	12	42	99	13.1
4	ZnNC-1100	5	12	12	97	9.3
5	Zn@C	5	12	2.1	60	2.8
6	N-C	5	12	5.2	39	1
7	ZIF-8	5	12	4.3	34	0.5
8	Zn(NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O	5	12	2.1	37	0.2
9	ZnO	5	12	3.3	59	0.1
10	blank	5	12	trace	trace	
11 <sup>[c]</sup>	blank	5	3	91	98	-
12	ZnNC-1000	16	3	67	84	20.9
13	ZnNC-1000	16	4	86	87	26.9
14	ZnNC-1000	16	5	94	95	29.4
15	ZnNC-1000	16	6	100	96	31.3

[a] Reaction conditions: nitrobenzene (0.5 mmol), FA (x equivalent), catalyst 20 mg, 150 °C, 2 mL THF, t h under Ar atmosphere. [b]Conversion was determined by GC. [c] 0.5 mmol aniline was used as the substrate.

Finally, the effect of employed FA amount on the catalytic performance was investigated. It should be noted that 4 equivalents of FA were needed when one mole nitrobenzene was converted to N-phenylformamide. Surprisingly, when 4 equivalents of FA were used, 86% conversion of nitrobenzene with 87% selectivity of N-phenylformamide was obtained (entry 13 and Figure S11). Further increase the amount of FA, both the conversion and selectivity were increased (entry 14 and 15). 100% conversion of nitrobenzene with 96% selectivity of N-phenylformamide was obtained when 6 equivalents of FA

were used (entry 15), indicating ZnNC-1000 exhibited a good FA utilization efficiency. Moreover, the present ZnNC-1000 catalyzed protocol was also effectively on a 10 mmol scale. 98% yield (GC) and 96% isolated yield was obtained with 0.96 mol% Zn and 6 equivalents FA at 150 °C (Scheme S1).

To get insights into the high performance of ZnNC-1000, we correlated the surface area and nitrogen content with the conversion of nitrobenzene respectively (Figure S12 and S13). However, non-linear relationship was obtained, indicating the surface area and nitrogen content could not play a decisive role on the catalytic performance over ZnNC-T samples. To further investigate the structure-activity relationship of ZnNC-T catalysts,  $H_2-D_2$ exchange reaction and HCOOH chemisorption tests were carried out over ZnNC-T and control samples. The rate of HD formation normalized by the mass of used catalysts is showed in Figure 3a. The control samples NC and Zn@C without N or Zn displayed moderate HD formation rate, indicating that both N and Zn played a crucial role in the hydrogen activation. Among the pyrolysis product ZnNC-T samples (ZnNC-800, -900, -1000 and -1100), the H<sub>2</sub> activation activity was first increased with the increase of pyrolysis temperature. When the pyrolysis temperature was increased up to 1000 °C. ZnNC-1000 showed the highest activity. Then further increase the pyrolysis temperature, the H<sub>2</sub> activation activity of ZnNC-1100 was decreased. It is obvious that not only N, Zn, but also the pyrolysis temperature played significant role in the H<sub>2</sub> activation activity, i.e. Zn-Nx was probably the active sites for the hydrogen activation. In addition, this phenomenon is agreed well with the catalytic performance of ZnNC-T, indicating the hydrogen activation played an important role in the reaction process.



Figure 3. Hydrogen activation and HCOOH chemisorption tests. a)  $H_2\text{-}D_2$  exchange reaction b-d) HCOOH-TPD on N-C, ZnNC-800, ZnNC-900, ZnNC-1000, ZnNC-1100 and Zn@C at 150  $^\circ\text{C}$  normalized by mass of the used catalyst.

Then HCOOH chemisorption tests were conducted to explore the reason why ZnNC-1000 showed the highest catalytic performance (Figure 3b-d and S14). The HCOOH-TPD results showed that the adsorption amount of HCOOH over ZnNC-T samples follows the order of ZnNC-800 < ZnNC-1100 < ZnNC-900 < ZnNC-1000, reaching a maximum HCOOH adsorption for ZnNC-1000 (Figure 3b). During the

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HCOOH-TPD process, the signal ascribed to H<sub>2</sub> and CO<sub>2</sub> over ZnNC-1000 catalyst displayed highest amount than the other tested catalysts (Figure 3c and 3d). This trend not only agreed well with the catalytic performance in the reductive Nformylation reaction, but also consisted with the HD formation rate in the H<sub>2</sub>-D<sub>2</sub> exchange reaction. All these results demonstrated that the hydrogen activation, HCOOH adsorption and the reductive N-formylation reaction might be related with the important effect between atomically dispersive Zn species and N-doped carbon, that is, the same active sites of Zn-Nx species in those catalysts. In addition, according to the XPS analysis, all ZnNC-T samples possessed the Zn-Nx species, and the relative content Zn-Nx was decreased in the following order ZnNC-800 (26.2%) > ZnNC-1000 (23.1%) > ZnNC-900 (21.7%) > ZnNC-1100 (21.4%). Therefore, based on the above results, we conclude that the pyrolysis temperature affects the structure and composition of the catalyst, resulting in the excellent catalytic performance of ZnNC-1000.

 Table 2. Comparison of Heterogeneous Catalysts for the for the reductive

 N-formylation of nitroarene

	NO <sub>2</sub> –	catalyst/Forimic T, t, 1 bar Ar o	acid ── <del>►</del> r N <sub>2</sub>	2a	H N O	
Entry	Catalyst	amount	T/ºC	h	Yield	Ref.
1	ZnNC-1000	3.2 mol%	150	16	96%	This worl
2	Co@NPC- 800	4.8 mol%	120	12	99%	7b
3	CoNC-700 <sup>a</sup>	1 mol%	110	5	98%	7h
4	Co@CN-800	16 mol%	110	12	92%	16
5	Co-Nx/C-800- AT <sup>b</sup>	0.17%	110	12	99%	2e

5	Co-Nx/C-800- AT <sup>b</sup>	0.17%	110	12	99%	2e
6	Pd-C	1.88 mol%	95	14	70%	15a
7	Mag-IL-Pd	0.25 mol%	90	24	97%	15b
8	Pd@PS⁰	8 mol%	135	20	86%	15c
9	Pd/ZnO	9.25×10 <sup>-9</sup> mol%	90	3.3	68%	15d
10	Au/rutile	1 mol%	70	2	99%	15e

<sup>a</sup>2-Nitrotoluene <sup>b</sup>2 MPa N<sub>2</sub>, <sup>c</sup>oxalic acid dihydrate was used.

To verify the occurrence of heterogeneous catalysis on ZnNC-1000, the filtration test was conducted at about 42% conversion of nitrobenzene. After remove of ZnNC-1000 catalyst, no further production can be detected even prolong the reaction time to 10 h under the same reaction conditions, implying that the reaction should be truly took place on the surface of heterogeneous catalysts. More importantly, the catalytic activity and the structure of the ZnNC-1000 could be well maintained after four runs, indicating good recyclability

and stability of ZnNC-1000 (Figure S15 and S16). The XRD pattern for ZnNC-1000 after reaction was like the fresh catalyst and no diffraction peaks corresponding to Zn or ZnO species was observed (Figure S17). In addition, no Zn particles was observed in the HRTEM image of the used catalyst (Figure S18). Encouraged by the above superior performance of ZnNC-1000 toward the catalytic reductive N-formylation of nitrobenzene, we subsequently investigated the substrate scope to explore the general applicability of this catalytic protocol under the optimized conditions. To our delight, some good or excellent results can be achieved, indicating the good substrate tolerance of the catalyst (Table S4). In addition, the reductive N-formylation of nitroarene were mainly performed with noble metal-based (such as Pd and Au) heterogeneous catalysts by using formic acid as the reductant and formylation reagent (entries 6-10, Table 2)<sup>[15]</sup>. To date, there is only a few examples of the reductive N-formylation of nitroarenes over the non-noble metal catalysts (entries 1-5, Table 2)<sup>[2e, 7b, 7h, 16]</sup>. To our delight, the catalytic activity of ZnNC-1000 was even comparable with the previous non-noble transition metal catalysts. All these results demonstrated that the atomically dispersed Zn-N<sub>x</sub> sites in the 3D N-doped carbon framework displayed excellent catalytic performance for reductive Nformylation of nitroarenes using FA.

Given all control experiments, we proposed plausible reaction mechanism as shown Scheme S2. In the first step, electronegative nitrogen atoms in ZnNC-1000 catalyst capture H<sup>+</sup> from formic acid to generate NH<sup>+</sup> and Zn-formate intermediate are also formed. In the second step, the Zn-formate intermediate can produce a CO<sub>2</sub> molecule and in situ form zinc-hydride species (ZnH<sup>-</sup>). Then when the nitroarene is added in the catalytic system, the generated NH<sup>+</sup> and ZnH<sup>-</sup> prefer to react with the nitro groups to form aniline. Finally, aniline reacted with formic acid quickly and generate the final product N-phenylformamide.

In summary, we described an efficient and eco-friendly ZnNC-1000 catalyst for the catalytic reductive N-formylation of nitroarenes with FA as the hydrogen source and formylation agent. It is  $Zn-N_x$  species in such catalysts that are responsible for the reductive N-formylation reaction, which are confirmed by the H<sub>2</sub>-D<sub>2</sub> exchange reaction and HCOOH chemisorption tests. In addition, the catalyst displays high FA utilization efficiency, wide substrate scope and good recyclability. This work opens new opportunities for the application of efficient, stable and low-cost transition metal single-atom catalysts.

#### **Experimental Section**

Experimental details are given in Supporting Information

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**Keywords:** zeolitic imidazolate framework • N-doped carbon • single atom catalysis • hydrogen activation • reductive Nformylation

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# COMMUNICATION

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Atomically dispersed zinc catalyst (ZnNC) derived from ZIF-8 possesses high surface area, moderate pore size, high zinc loading (5.12 wt%) and nitrogen content (6.73 wt%), which provide abundant active sites. Thanks to the highest activation activity for HCOOH, the optimized ZnNC-1000 shows the unique catalytic performance for the one-pot reductive N-formylation of nitroarene with HCOOH as the hydrogen donor and formylation agent.



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Atomically Dispersed Zn-Nx Sites in N-Doped Carbon for Reductive Nformylation of Nitroarenes with Formic Acid