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# Cobalt encapsulated in N-doped graphene sheet for one-pot reductive amination to synthesize secondary amines

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ARTICLE INFO	A B S T R A C T		
Keywords: Nitro compounds Carbonyl compounds Reductive amination Co catalyst	To develop an efficient base-metal reductive amination catalyst for synthesis of secondary amines is still a major challenge. In this study, an efficient N-doped graphene sheet-coated cobalt catalyst (Co@CN-800) was developed through a simple pyrolysis process, which could gave 99.5 % yield of N-benzylaniline by one-pot reductive amination of nitrobenzene with benzaldehyde during at least 5 cycles. Catalyst characterization and control experiments confirmed that the robust catalytic performance of the catalyst is probably due to the synergy effect of in situ generated Co-Nx encapsulated in N-doped graphene layer and appropriate meso-pore structure. Additionally, The substrate adaptability of the catalyst was proved since a variety of corresponding secondary amines were smoothly obtained under relatively mild conditions, which makes the secondary amine synthesis strategy based on Co@CN-800 shows excellent application prospect.		

# 1. Introduction

Secondary amine is an important class of fine chemicals, which has a wide range of applications in the field of pharmaceutical, agrochemical, and functional material [1]. Traditionally, N-alkylation of primary amines, alkylation of amines, reduction of amides, addition reactions to imines, and the reductive amination, have been adopted for the synthesis of secondary amines [2–4]. Although most of these methods shown to be effective, the one-pot reductive amination of nitro compounds with aldehydes or ketones has become one of the most promising green synthesis methods due to the advantages of readily available substrates and high atom economy.

Up to now, the one-pot reductive amination has been examined via the process of catalytic hydrogenation under the  $H_2$  atmosphere or catalytic transfer hydrogenation (CTH) with hydrogen donors (formic acid, isopropanol, etc.) [5–8]. Although the CTH process has made well progress, the existence of an additional hydrogen donor or base would inevitably bring its by-product, which may cause environmental pollution or bring difficulties to the purification of products. Therefore,  $H_2$  is still a more attractive and cleaner reductant, so the reductive amination reaction under  $H_2$  atmosphere to prepare secondary amines is of great significance in both academic research and industrial production. Although many kinds of literatures have reported that secondary amines could be efficiently synthesized via the one-pot reductive amination reaction in the presence of hydrogen, there are still many shortcomings in the current method such as the limited substrates, poor activity, and expensive noble-metal catalysts [9–11].

In recent years, many attempts have been focused on the fabrication of hydrogenation catalysts with base metals [12–14]. The problem that often arises is that the activity of this type of catalyst cannot catch up with the noble metal catalyst, and thus more severe reaction conditions are often applied [15,16]. Another problem worth mentioning is the poor stability due to possible poisoning of the catalyst by coordination of nitrogen atoms with metal nanoparticles (NPs) [17]. To overcome these questions, the encapsulation of metal nanoparticles into nitrogen-doped porous carbon shell is a promising strategy, which can enhance the stability and dispersion of the metal NPs through the confinement effect of the carbon material [18–20].

Recently, the transition metal, especially Co encapsulated in N doped carbon matrix has been developed for various reactions, such as: catalytic hydrogenation, ORR, etc. [21–24]. Although these catalysts have shown excellent catalytic performance for the conversion of nitrobenzene to aniline, there are few reports on the one-pot synthesis of secondary amines under the  $H_2$  atmosphere. As is widely accepted, three tandem reactions such as the hydrogenation of the corresponding nitro compounds, condensation of the amine with an aldehyde (ketones) to

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imine, and the hydrogenation of imine to expected secondary amine are needed for the amination of nitro compounds and aldehydes (ketones). The hydrogenation and amination of aniline are easy to carry out, while the selective hydrogenation of C—N bond in benzylidene aniline is more difficult to carry out due to the conjugation effect of C—N with the benzene ring, which makes the tandem reactions of reductive amination more complex than the extensively studied hydrogenation of nitroarenes to aromatic amines, and harsh conditions are often adopted [25]. For example, Matthias Beller et al. developed an efficient Co catalyst, which exhibits well activity for the synthesis of secondary amines, but the reaction  $H_2$  pressure was as high as 40 bars [26]. Therefore, it is still highly attractive to design an efficient non-noble metal catalyst for reductive amination reaction.

Based on the above considerations, Co encapsulated in N-doped graphene sheet catalyst was built via a facile pyrolysis strategy in the present studies. The obtained catalyst is carefully investigated with various characterizations, and further applied to the reductive amination reaction of nitroarenes and aldehydes. The obtained results demonstrated that the hybrids can serve as an efficient and robust catalyst for synthesis of secondary amine via one-pot reductive amination.

# 2. Experimental

# 2.1. Materials

 $Co(NO_3)_2 \cdot 6H_2O$  was provided by Macklin Biochemical Co., Ltd. (Shanghai, China). Melamine and glucose were purchased from Tianjin Kermel Co., Ltd. (China). Methanol and other reaction solvent were purchased from Tianjin Fuyu Fine Chemical Industry Co., Ltd. (China). The reaction substrate including nitroarenes and aldehydes were supplied by Shanghai Macklin Biochemical Co., Ltd. (China). All the reagents and chemicals were used directly without any further purification.

## 2.2. Catalyst preparation

The Co@CN-*x* catalyst was prepared by a two-step pyrolysis process under N<sub>2</sub> atmosphere as shown in Scheme 1. In a typical synthesis procedure, 1.846 g Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in a beaker containing 150 mL of methanol, and then 4.0 g glucose was slowly added thereto. After ultrasonic dispersion fully, 20 g melamine was added into the above system. The mixture was ultrasonically dispersed for another 2 h. And then the solvent was removed by evaporation under 80 °C in a water bath. The obtained precursor was then placed in a quartz boat and pyrolyzed at different temperature (700, 800, and 900 °C) under N<sub>2</sub> atmosphere at a ramp rate of 2 °C min<sup>-1</sup> to 600 °C and keep for 1 h, and the temperature was further raised to the target temperature at a ramp rate of 2 °C min<sup>-1</sup> and keep for 2 h. The obtained powder was named Co@CN-*x* (*x* refers to the pyrolysis temperature).

## 2.3. Catalyst characterization

Powder X-ray diffraction patterns (XRD) were acquired on a Smart Lab using a Cu K $\alpha$  radiation (45 kV, 200 mA). X-ray photoelectron spectroscopy (XPS) was measured on a Thermo Escalab Xi<sup>+</sup> Spectrometer with a monochromated Al K $\alpha$  X-ray resource, and C 1s at 284.4 eV was used as a reference for all binding energies. The texture properties were studied by the Brunanuer-Emmett-Teller (BET) method via the ASAP-2460 physical adsorption instrument. Raman spectra were recorded on Renishaw in Via Raman spectrometer. The transmission electron microscopy (TEM) images were performed on Talos F200x operating at 200 kV. The elemental analysis was carried out in the Elementar Vario EL analyzer. Quantitative determination of cobalt in the catalyst was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, PerkinElmer instruments, Norwalk, 2100DV, USA)

# 2.4. Catalytic test

The reaction was carried out in a 75 mL 6-channel Parr autoclave. In a typical experiment, nitrobenzene (1 mmol), benzaldehyde (2 mmol), catalyst (12 mg), and methanol (10 mL) were charged into the reactor. The autoclave was purged with H<sub>2</sub> 3 times to remove air, and then pressurized to 2 MPa with H<sub>2</sub>, followed by heating to 150 °C. Subsequently, the reaction was kept under a magnetic stirring rate of 400 rpm for 6 h. After cooling to room temperature, the residual H<sub>2</sub> was released, and the obtained liquid solution was analyzed by GC with toluene as the internal standard (Agilent 7890 B, SE-30 column). The obtained Products were confirmed by GC–MS (Agilent 7890A GC/5975C MS, HP-5 column). After the completion of the reaction, the catalyst was recovered using an external magnet and washed with methanol for next cycle.

## 3. Results and discussion

## 3.1. Characterization

N2 adsorption-desorption isotherm was implemented to investigate the detailed porous features and textural properties of the as-prepared Co@CN-x catalysts, as shown in Fig. 1. The N2 isotherms of Co@CN-700 could be classified as typical type-I characteristics, which occurred dramatic absorption at a lower relative pressure, manifesting the existence of numerous micropores. While Co@CN-700 and Co@CN-800 showed a type-IV isotherm, which indicated that the mesoporous structure nature of these catalysts. As shown in Table S1, the specific surface area of the catalyst greatly changed with the pyrolysis temperatures. Relatively larger surface areas are obtained with 362.9 and 221.8 m<sup>2</sup>/g for Co@CN-800 and Co@CN-900 catalysts, respectively, whereas a low value of 70.7  $m^2/g$  is observed on the Co@CN-700 catalyst. The specific surface area and the pore volume of Co@CN-800 were larger than that of most of the carbon-based Co catalysts reported in previous studies [27]. Such a high surface area and porous structure conducive to providing sufficient mass transfer and expose extensive active sites and



Scheme 1. Diagram for the fabrication of Co@CN-x.



Fig. 1.  $\rm N_2$  sorption isotherms of (a) Co@CN-700, (b) Co@CN-800, (c) Co@CN-900.

affords sufficient diffusion space for reactants during the reaction and thus promoting significantly its catalytic performance.

As shown in Fig. 2, all the catalysts exhibited a broad diffraction peak of (002) reflection of carbon at around 26.2°. No obvious Co diffraction lines were collected on the XRD spectra of Co@CN-700, which indicated that at low pyrolysis temperatures, the catalyst precursor likely not be efficiently pyrolyzed. This is also consistent with the previous N<sub>2</sub> sorption characterization results. While at higher pyrolysis temperature, new diffraction peaks at 44.1°, 51.4°, and 75.8° were observed, which are corresponded to (111), (200), and (220) lattice planes of metallic Co, respectively [28,29]. These results demonstrated that higher pyrolysis temperature is beneficial to the crystallization and reduction of Co precursor, which is also consistent with previous literature [30].

As shown in Fig. 3a–c, the mean size of Co NPs varies with the increases of pyrolysis temperature from 700 to 900 °C, and is consistent with the result obtained by XRD characterization before (ESI, Table S1). The obvious agglomeration of Co NPs was observed on Co@CN-900, which indicated that too high pyrolysis temperature was not beneficial to control the particle size of Co species. According to the HRTEM image of Co@CN-800 (Fig. 4d), the lattice distances of cores and shells are 0.203 nm and 0.34 nm, respectively, which are attributed to the (111) planes of metallic Co and the (002) plane of graphite [31]. These results



Fig. 2. XRD patterns of (a) Co@CN-700, (b) Co@CN-800, (c) Co@CN-900.

indicated that most of the metallic Co NPs are well embedded in the graphite layer. Besides, some defects were observed on the carbon layer at the periphery of the Co active component (Fig. 3e, f), and these defects can serve as reaction channels, thereby promoting the catalytic reaction [21].

The XPS survey of Co@CN-x confirmed the existence of Co, C, N, and O elements in these catalysts (Fig. S1). The content of Co from XPS is lower than that from by ICP-AES, and the content of C and N obtained by XPS is higher than that obtained by an organic element analyzer (Table S2). This further supported the results obtained by TEM, that is, Co species were coated inside the nitrogen-doped carbon material. The C1s spectra of Co@CN-x (Fig. S2) showed that, the C1s peak becomes more and more sharp with the increase of pyrolysis temperature. The peak splitting results further confirmed that the composition of graphene carbon gradually increases (Table S3). This shows that higher temperature is conducive to the formation of graphene carbon, which is consistent with the previous results [30]. The N 1s spectra of Co@CN-x (Fig. 4) can be fitted into pyridinic-N, Co-Nx, pyrrolic-N, graphitic-N, and oxidized-N, respectively [32,33]. It was well accepted that the pyridine-type N species could function as the anchor to stabilize the metal NPs [34]. As the pyrolysis temperature increases, the proportion of graphitic-N and oxidized-N in these Co@CN-x samples increase significantly, but even the catalysts pyrolyzed at 900 °C still have a relatively high proportion of pyridinic-N (Table S4). This is probably the reason why the catalyst in this study has a smaller particle size of the Co NPs as shown in Fig. 3a-c.

As depicted in Fig. 5, the Co  $2p_{3/2}$  spectrum can be deconvolved into four peaks, such as metallic Co, Co-Ox, Co-Nx, and the "shake up" peak, respectively (Fig. 5) [6]. The proportions of metallic Co increased significantly with the increases of pyrolysis temperature, while the proportions of Co-Ox and Co-Nx decreased, accordingly (Table S4). Considering both the quantitative results and the catalyst preparation process, it suggested that Co-Ox species were first formed, followed by Co-Nx upon substitution O with N, and finally, the special Co NPs encapsulated in N-doped carbon layers catalyst was obtained [35,36]. It needs to be pointed out that the Co-Nx species still has a high proportion in the catalyst (about 22.7 % for Co@CN-800), and some studies also suggested that Co-Nx species often play a key role in the catalytic hydrogenation [37].

As manifested in Raman spectra of these catalysts (Fig. 6), the G and D bonds were identified for all catalysts, which can be assigned to the tangential stretching of C—C bonds and graphitic defects, respectively [38]. The  $I_D/I_G$  value increases with the increase of pyrolysis temperature, which indicates the increase of in the graphitization degree of the catalyst (Table S1). Also, the typical characteristic peaks of Co-Ox at 469, 513, 617, and 675 cm<sup>-1</sup> as shown in Fig. 6(a, b), and there is no obvious peak in the Raman spectrum of Co@CN-900, which may be due to the decomposition of Co-Ox and to form metallic Co at higher pyrolysis temperature [39]. These results were consistent with the results from XPS characterizations (Fig. 5 and Table S5).

## 3.2. Catalytic activity

The one-pot reductive amination of nitrobenzene with benzaldehyde was investigated as a model reaction for catalyst screening. As shown in Table 1, this reaction cannot be carried out normally in absence of a catalyst (Entry 1 in Table 1). CN-800 was not active for the model reaction also, indicating that Co is essential for the construction of reductive amination catalyst (Entry 2 in Table 1). Although the conversion of nitrobenzene reached 1.0 % under the same reaction conditions, the selectivity of the target product given by the catalysts obtained at different pyrolysis temperatures was quite different (Entry 3–5 in Table 1). Co@CN-700 only gave a 36.7 % selectivity to N-benzylaniline, while the intermediate N-benzylidene aniline was the main product. As the catalyst pyrolysis temperature increased to above 800 °C, the selectivity of N-benzylaniline increased to 53.4 %, and then down to



Fig. 3. TEM image of (a) Co@CN-700, (b) Co@CN-800, (c) Co@CN-900 and HTEM image of Co@CN-800 (d-f).



Fig. 4. The N 1s spectra of (a) Co@CN-700, (b) Co@CN-800, (c) Co@CN-900.

21.0 %. It is well accepted that the reductive amination of benzaldehyde and nitrobenzene undergoes the following scheme as depicted in Table 1. According to the above reaction results, it can be inferred that the hydrogenation of the C=N bond in N-benzylidene aniline is the key step affecting the total reductive amination process due to the conjugation effect with the benzene ring.

Combined with the previous  $N_2$  sorption and XRD results (Figs. 1 and 2), the poor activity of Co@CN-700 may be due to the low pyrolysis temperature limits the in-situ reduction of Co-Ox and the formation of mesoporous structure. Because the quite low content of active Co species



Fig. 5. The Co  $2p_{3/2}$  spectra of (a) Co@CN-700, (b) Co@CN-800, (c) Co@CN-900.

in this catalyst was almost wrapped in the nitrogen-doped carbon, and the poor pore structure of the catalyst restricted the contact between the reactants and the active component. Although a high pyrolysis temperature was considered to enhance the reduction of Co-Ox and the exposure of the active sites due to the formation of excellent mesoporous structures. However, too high a temperature will cause the collapse of the pore structure and the agglomeration of metal components as previously revealed by  $N_2$  sorption (Fig. 1 and Table S1) and TEM images (Fig. 3). This may be the reason why the activity of the Co@CN-900



**Fig. 6.** The Raman spectra of (a) Co@CN-700, (b) Co@CN-800, (c) Co@CN-900.

catalyst is lower than that of Co@CN-800. Based on the above results, it can be confirmed that 800 °C was the optimal pyrolysis temperature to generate a porous structure with highly dispersed small size Co species.

Once the optimal pyrolysis temperature was obtained, the reaction conditions were optimized to further reveal the activity of Co@CN-800. As shown in Table 1, the catalytic activity of the Co@CN-800 depends on the pressure of feeding H<sub>2</sub>, e.g., the yield of the N-benzylaniline increased to 74.5 % and 93.0 % with the increasing of H<sub>2</sub> pressure increased to 1.5 and 2 MPa, respectively (Entry 6, 7 in Table 1). Considering the safety of the experiment, 2.0 MPa was selected as the optimal reaction pressure. The reaction temperature is another important factor affecting the catalytic activity. As it was lowered to 110 °C, the selectivity of the product was only 39.9 %, while when the reaction temperature was elevated to 150 °C, the selectivity of the product was close to 100 % (Entry 7–9 in Table 1).

To evaluate whether the catalyst can be used in the industry, the stability test was firstly examined at low conversion. As depicted in Fig. 7, the conversion of nitrobenzene is stable at about 52 % in the

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process of five consecutive cycles. Unfortunately, the desired product was not detected in the reaction mixture and almost 100 % imine (N-benzylidene aniline) was obtained. This further shows that the difficulty of this reductive amination reaction lies in the hydrogenation of C = N in N-benzylidene aniline. In order to further investigate the stability of Co@CN-800, a more severe reaction condition was applied. Although the imine (N-benzylidene aniline) was still the main product, the yield of the target product did not change significantly during five consecutive cycles (Fig. 8). The stability experiment results obtained under the optimal reaction conditions further confirmed the robustness of Co@CN-800 (Fig. S3).

To better explore its stability, the spent Co@CN-800 catalyst was characterized after eluted with ethanol. It can be seen from the XPS spectrum of the spent catalyst, the carbon species did not change significantly (Fig. S2, Table S3), obviously metal species leaching was not found, and the chemical environment of Co on the catalyst did not change significantly (Fig. S4, and Table S5). The elemental analysis results demonstrated that the proportion of nitrogen slightly increased,



Fig. 7. Recycle of Co@CN-800 at low conversion (Reaction conditions: nitrobenzene, 1 mmol; benzaldehyde, 2 mmol; catalyst dosage, 12 mg; temperature, 90 °C; time, 2 h;  $H_2$  pressure, 1 MPa.).

## Table 1

The results of the one-pot reductive amination reaction.

NO <sub>2</sub> +	CHO Pressure, catalyst Temperature	+					
		Intermediate product	Target product				
Entry	Catalyst	Temp. (°C)	H <sub>2</sub> (MPa)	Time (h)	Solvent	Conv. (%)	Sel. %)
1	No catalyst	130	1	6	MeOH	_	-
2 <sup>a</sup>	CN-800	130	1	6	MeOH	5.7	0
3	Co@CN-700	130	1	6	MeOH	100	36.7
4	Co@CN-800	130	1	6	MeOH	100	53.4
5	Co@CN-900	130	1	6	MeOH	100	21.0
6	Co@CN-800	130	1.5	6	MeOH	100	74.5
7	Co@CN-800	130	2	6	MeOH	100	93.0
8	Co@CN-800	110	2	6	MeOH	100	39.9
9	Co@CN-800	150	2	6	MeOH	100	99.5
10 <sup>b</sup>	Co@CN-P	150	2	6	MeOH	100	64.5
11 <sup>c</sup>	Co@CN-A	150	2	6	MeOH	100	99.6
12	Co@C-800	150	1	6	MeOH	30.3	18.4
13	Co@N-800	150	2	6	MeOH	100	99.6

Reaction conditions: nitrobenzene (1 mmol), benzaldehyde (2 mmol), catalyst dosage 12 mg, solvent (10 mL).

<sup>a</sup> Obtained by pyrolysis of melamine and glucose.

<sup>b</sup> The catalyst was poisoned with 4 Equiv. of KSCN.

 $^{\rm c}\,$  The catalyst was soaked in 1 M HCl acid for 48 h before use.



Fig. 8. Recycle of the Co@CN-800 at low yield (Reaction conditions: nitrobenzene, 1 mmol; benzaldehyde, 2 mmol; catalyst dosage, 12 mg; temperature, 130 °C; time, 5 h; H<sub>2</sub> pressure, 1 MPa.).

Sel. (%)

99.5

94.5

93.3

96.4

95.4

93.0

95.4

98.0

98.6

93.6

87.3

98.8

97.7

which might be because the ethanol elution could not completely remove the reaction substrate or products adsorbed on the catalyst (Table S2). However, the proportion of N species on the catalyst did not change significantly, which further confirmed the excellent stability of the catalyst (Fig. S5, Table S4). Also, the XRD results showed no perceptible structural change was observed on spent Co@CN-800, and the average particle size of Co NPs did not change obviously (Fig. S6). Thus, the above characterization results further confirmed the stability of the obtained Co@CN-800 catalyst.

Although the coordinated Co-Nx site rather than metallic Co was claimed to be the main active site towards the hydrogenation of nitro group, the catalytic effect of the Co-related active sites for the present reductive amination reaction is still unrevealed [5]. To identify the catalytic active sites of the present reaction, a widely used metallic Co KSCN pre-poisoning experiment was performed [40]. It was found that the proportion of different Co species in the poisoned Co@CN-800 catalyst (Named Co@CN-P) did not change significantly, but the binding energy of metallic Co species slightly increased when compared to Co@CN-800 catalyst (Fig. S7 and Table S4), which confirmed the formation of strong coordination bond between the metallic Co and the added  $SCN^{-}$  ions [41]. It can be seen from the reaction results that the catalyst still gives 100 % conversion of nitrobenzene (Entry 10 in

Table 2			
One-pot reductive amination	with substituted nitro	and carbonyl	compounds.

1

2

3

4

5

6

7

8

9

10

11

12

13

Nitro compound Carbonyl compound Entry Product Conv. (%) > 99.9 > 99.9 > 99.9 > 99.9 > 99.9 сно > 99.9 сно > 99.9 CHO. > 99.9 > 99.9 сно > 99.9 CHO. > 99.9 > 99.9 сно > 99.9 сно > 99.9

14 86.7 15 CHO. > 99.9 95.6 16 NO. CHO. > 99.9 93.0 17 CHO. > 99.9 93.0

Reaction conditions: nitro compound (1 mmol), carbonyl compound (2 mmol), MeOH (10 mL), catalyst dosage (10 % of the weight of nitro compounds), 150 °C, 2 MPa H<sub>2</sub>, 6 h.

Table 1), which shows that the Co-Nx species is still the active center of hydrogenation of nitro compounds during the reductive amination reaction. Although the selectivity of the target product was lower than that of the original Co@CN-800, the yield of N-N-benzylaniline can still reach more than 60 % (Entry 10 in Table 1). Since Co has been poisoned by SCN<sup>-</sup>, Co-Nx is likely to be the active center for the hydrogenation of C=N bond in N-benzylidene aniline, and the decreases of selectivity may be due to the plugging of the pore channels of the catalyst by the added SCN<sup>-</sup>. To further confirm this conclusion, the fresh Co@CN-800 catalyst was treated with 1 M HCl to remove the metallic Co species (Named Co@CN-A). It can be seen from the ICP-AES characterization results that the Co content on the catalyst decreased sharply to 65 % of the original content. XPS results show that the proportion of metallic Co is significantly reduced, and the proportion of Co-Nx is doubled (Fig. S7, and Table S4). The reaction results showed that the catalyst could still give a catalytic performance like that of Co@CN-800 (Entry 11 in Table 1), which further confirmed that Co-Nx was more likely to be the main active site of the present reaction than metallic Co.

As shown in Scheme 1, melamine, glucose, and Co precursors were added during the preparation of the catalyst. To better reveal their role, several control experiments were performed. Firstly, an N-free catalyst namely Co@C-800 was prepared following the same procedure with Co@CN-800, just without melamine added. As can be seen from Table S2, the Co content of the catalyst is higher than that of Co@CN-800, but N content is lower than 1 % (The residual N may be due to the introduction of the nitro group in the precursor). It can be seen from Fig. S8, no Co-Nx species were observed from the Co 2p spectra of Co@C-800, and Co existed mainly in the form of metallic and oxidation state. According to the deconvolution result based nonlinear leastsquares fitting routines (NLSF), the content of the metallic Co on the catalyst can reach 57.6 %, which is much higher than that of Co@CN-800. However, the catalyst only gave a conversion of 30 % under the same reaction conditions (Entry 12 in Table 1). This further proves that Co-Nx is the main active site of the catalyst. It can therefore be concluded that melamine is indispensable in the catalyst preparation process. Co@N-800 catalyst was also prepared without the addition of glucose. As shown in Table 1, the catalyst has a similar catalytic activity to the Co@CN-800 catalyst, but a rapid deactivation was observed when the catalyst was recycled four times (Entry 13 in Table 1). This may be due to the loss of the protection of the carbon shell in the Co active center, which reduces its stability. In summary, the excellent catalytic activity of Co@CN-800 is the result of the synergistic effect of glucose and melamine in the precursor.

The general scope of Co@CN-800 for the synthesis of secondary amines was investigated via various nitroarenes and aldehydes, and the structure of the target product was confirmed by GC-MS. Firstly, the reductive amination of nitrobenzene with different aldehydes was studied. Regardless of whether the substituent of the aromatic aldehyde is an electron-withdrawing group or an electron-donating group, it can react smoothly with nitrobenzene to generate the target amine with excellent yield (Entries 2-4). It is noteworthy that heteroaromatic aldehydes (4-pyridine carboxaldehydes) can also be efficiently converted to the corresponding secondary amines (Entry 5). It is more challenging to use aliphatic aldehydes in one-pot reductive amination reactions. As shown in Table 2 (Entries 6–8), our method is also effective for aliphatic aldehydes, and the corresponding secondary amines were received in yield of 93.0 %, 95.4 %, and 98.0 % respectively. To further reveal the scope of the catalyst, various nitroarenes were also explored. As shown in Table 2 (Entries 9-17), the reductive amination reaction can still proceed well. Even if there is a strong electron-withdrawing group -CN on the molecule, the yield of the target amine is close to 90 % (Entry 14). Therefore, the developed Co@CN-800 not only exhibits excellent catalytic performance but also good applicability and tolerance to various reaction substrate.

## 4. Conclusions

A robust Co@CN-800 catalyst was successfully fabricated for a onepot reductive amination reaction by a simple pyrolysis method, which shows excellent activity and stability due to the special core-shell structure and the high proportion of Co-Nx. Also, the present catalytic system has excellent substrate adaptability which makes the method of synthesizing secondary amine by one-pot reductive amination based on the Co@CN-800 catalyst have important application prospect.

## CRediT authorship contribution statement

Lin Liu: Data curation, Writing - original draft. Wenxiu Li: Investigation, Writing - original draft. Ran Qi: Data curation, Investigation. Qingqing Zhu: Writing - review & editing. Jing Li: Writing - review & editing. Yuzhen Fang: Writing - review & editing. Xiangjin Kong: Supervision, Writing - review & editing, Project administration.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2021.111504.

## References

- Anne Schuhmacher, Tomoya Shiro, Sarah J. Ryan, Jeffrey W. Bode, Synthesis of secondary and tertiary amides without coupling agents from amines and potassium acyltrifluoroborates (KATs), Chem. Sci. 11 (2020) 7609–7614.
- [2] Elena Petricci, Niccolò Santillo, Daniele Castagnolo, Elena Cini, Maurizio Taddei, Ironcatalyzed reductive amination of aldehydes in isopropyl alcohol/water media as hydrogen sources, Adv. Synth. Catal. 360 (2018) 2560–2565.
- [3] Dian Deng, Yusuke Kita, Keigo Kamata, Michikazu Hara, Low-temperature Reductive amination of carbonyl compounds over Ru deposited on Nb<sub>2</sub>O<sub>5</sub>•nH<sub>2</sub>O, ACS Sustain. Chem. Eng. 7 (5) (2018) 4692–4698.
- [4] Liang Jiang, Peng Zhou, Zehui Zhang, Quan Chi, Shiwei Jin, Environmentally friendly synthesis of secondary amines via one-pot reductive amination over a heterogeneous Co-Nx catalyst, New J. Chem. 41 (20) (2017) 11991–11997.
- [5] Haotian Guo, Ruixiao Gao, Mingming Sun, Hao Guo, Bowei Wang, Ligong Chen, Cobalt entrapped in N, S-Codoped porous carbon: catalysts for transfer hydrogenation with Formic Acid, ChemSusChem. 12 (2) (2019) 487–494.
- [6] Man Yuan, Yu Long, Jin Yang, Xiwei Hu, Dan Xu, Yangyang Zhu, Zhengping Dong, Biomass sucrose-derived Cobalt@Nitrogen-doped carbon for catalytic transfer hydrogenation of nitroarenes with formic acid, ChemSusChem 11 (23) (2018) 4156–4165.
- [7] Xueliang Cui, Kun Liang, Meng Tian, Yangyang Zhu, Jiantai Ma, Zhengping Dong, Cobalt nanoparticles supported on N-doped mesoporous carbon as a highly efficient catalyst for the synthesis of aromatic amines, J. Colloid Interface Sci. 501 (2017) 231–240.
- [8] Qian Zhu, Xun Sun, Hong Zhao, Dan Xu, Zhengping Dong, Selective transfer hydrogenation and N-formylation of nitroarenes by a facilely prepared N, S Codoped carbon-encapsulated cobaltnanoparticle catalyst, Ind. Eng. Chem. Res. 59 (13) (2020) 5615–5623.
- [9] Derya Gülcemal, Süleyman Gülcemal, Craig M. Robertson, Jianliang Xiao, A new phenoxide chelated IrIII N-Heterocyclic carbene complex and its application in reductive amination reactions, Organometallics 34 (17) (2015) 4394–4400.
- [10] Linsen Li, Zhiqiang Niu, Shuangfei Cai, Yun Zhi, Hao Li, Hongpan Rong, Lichen Liu, Lei Liu, Wei He, Yadong Li, A PdAg bimetallic nanocatalyst for selective reductive amination of nitroarenes, Chem. Commun. 49 (2013) 6843–6845.
- [11] E.A. Artiukha, A.L. Nuzhdin, G.A. Bukhtiyarova, S. Yu Zaytsev, P.E. Plyusnin, Yu V. Shubin, V.I. Bukhtiyarov, One-pot reductive amination of aldehydes with

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nitroarenes over an  $Au/Al_2O_3$  catalyst in a continuous flow reactor, Catal. Sci. Technol. 5 (2015) 4741–4745.

- [12] Tobias Stemmler, Annette-Enrika Surkus, Marga-Martina Pohl, Kathrin Junge, Matthias Beller, Iron-catalyzed synthesis of secondary amines: on the way to green reductive aminations, ChemSusChem 7 (11) (2014) 3012–3016.
- [13] Jacky H. Advani, Krishnan Ravi, Dhanaji R. Naikwadi, Hari C. Bajaj, Manoj B. Gawande, Ankush V. Biradar, Bio-waste chitosan-derived N-doped CNTsupported Ni nanoparticles for selective hydrogenation of nitroarenes, Dalton Trans. 49 (2020) 10431–10440.
- [14] Kangkai Liu, Yueling Cao, Shaowei Yang, Chen Wu, Zhuorui Zhang, Qiuyu Zhang, Hepeng Zhang, Molybdenum carbide-promoted cobalt as an efficient catalyst for selective hydrogenation, Ind. Eng. Chem. Res. 59 (32) (2020) 14267–14277.
- [15] Yusuke Kita, Sayaka Kai, Lesandre Binti Supriadi Rustad, Keigo Kamata, Michikazu Hara, One-pot reductive amination of carbonyl compounds with nitro compounds over a Ni/NiO composite, RSC Adv. 10 (54) (2020) 32296–32300.
- [16] Kyungjun Kim, Dong Woo Kang, Youngheon Choi, Wanggyu Kim, Hyunjoo Lee, Jae W. Lee, Improved H2 utilization by Pd doping in cobalt catalysts for reductive amination of polypropylene glycol, RSC Adv. 10 (2020) 45159–45169.
- [17] Ruirui Yun, Shi Zhang, Wanjiao Ma, Xiao Lv, Shoujie Liu, Tian Sheng, Suna Wang, Fe/Fe<sub>3</sub>C encapsulated in N-doped carbon tubes: a recyclable catalyst for hydrogenation with high selectivity, Inorg. Chem. 58 (2019) 9469–9475.
- [18] Jiayi Li, Bowei Wang, Yutian Qin, Qin Tao, Ligong Chen, MOF-derived Ni@NC catalyst: synthesis, characterization, and application in one-pot hydrogenation and reductive amination, Catal. Sci. Technol. 9 (14) (2019) 3726–3734.
- [19] Haotian Guo, Bowei Wang, Pengzhi Qiu, Ruixiao Gao, Mingming Sun, Ligong Chen, N, S-Codoped carbon shells embedded with ultrafine Co NPs for reductive amination with formic Acid, ACS Sustain. Chem. Eng. 7 (2019) 8876–8884.
- [20] Jinlei Li, Guoliang Liu, Xiangdong Long, Guang Gao, Jun Wu, Fuwei Li, Different active sites in a bifunctional Co@N-doped graphene shells based catalyst for the oxidative dehydrogenation and hydrogenation reactions, J. Catal. 355 (2017) 53–62.
- [21] Zhongzhe Wei, Yiqing Chen, Jing Wang, Diefeng Su, Minghui Tang, Shanjun Mao, Yong Wang, Cobalt encapsulated in N-doped graphene layers: an efficient and stable catalyst for hydrogenation of quinoline compounds, ACS Catal. 6 (2016) 5816–5822.
- [22] You Lin Liu, Xue Yan Xu, Ping Chuan Sun, Tie Hong Chen, N-doped porous carbon nanosheets with embedded iron carbide nanoparticles for oxygen reduction reaction in acidic media, Int. J. Hydrogen Energy 40 (2015) 4531–4539.
- [23] Li Peng ShuliangYang, Safak Bulut EmadOveisi, Daniel T. Sun, Mehrdad Asgari, Olga Trukhina, Wendy L. Queen, MOF-derived cobalt phosphide carbon nanocubes for selective hydrogenation of nitroarenes to anilines, ChemPubSoc 24 (2018) 4234–4238.
- [24] Zhongzhe Wei, Jing Wang, Shanjun Mao, Diefeng Su, Haiyan Jin, Yihe Wang, Fan Xu, Haoran Li, Yong Wang, In situ-generated Co0-Co<sub>3</sub>O<sub>4</sub>/N-doped carbon nanotubes hybrids as efficient and chemoselective catalysts for hydrogenation of nitroarenes, ACS Catal. 5 (2015) 4783–4789.
- [25] Kathiravan Murugesan, Thirusangumurugan Senthamarai, Vishwas G. Chandrashekhar, Kishore Natte, Paul C.J. Kamer, Matthias Beller, Rajenahally V. Jagadeesh, Catalytic reductive aminations using molecular hydrogen for synthesis of different kinds of amines, Chem. Soc. Rev. 49 (17) (2020) 6273–6328.
- [26] Kathiravan Murugesan, Vishwas G. Chandrashekhar, Thirusangumurugan Senthamarai, Rajenahally V. Jagadeesh, Matthias Beller, Reductive amination using cobalt-based nanoparticles for synthesis of amines, Nat. Protoc. 15 (4) (2020) 1313–1337.

- [27] Ziliang Chen, Renbing Wu, Yang Liu, Yuan Ha, Yanhui Guo, Dalin Sun, Miao Liu, Fang Fang, Ultrafine Co nanoparticles encapsulated in carbon-nanotubes-grafted graphene sheets as advanced electrocatalysts for the hydrogen evolution reaction, Adv. Mater. 30 (2018), 1802011.
- [28] Peng Zhou, Liang Jiang, Fan Wang, Kejian Deng, Kangle Lv, Zehui Zhang, High performance of a cobalt-nitrogen complex for the reduction and reductive coupling of nitro compounds into amines and their derivatives, Sci. Adv. 3 (2017), e1601945.
- [29] Xiangjin Kong, Weijie Geng, Wenxiu Li, Lin Liu, Xiaoqi Yan, Longchen Gong, Junhai Liu, Co encapsulated N-doped carbon nanotubes as robust catalyst for valorization of levulinic acid in aqueous media, J. Energy Chem. 52 (2021) 12–19.
- [30] Wenxiu Li, Weijie Geng, Lin Liu, qianqian Shang, liying Liu, Xiangjin Kong, In Situgenerated Co embedded in N-doped carbon hybrids as robust catalyst for the upgrading of levulinic acid in aqueous phase, Sustain. Energy Fuels 4 (2020) 2043–2054.
- [31] Kangkai Liu, Yueling Cao, Shaowei Yang, Chen Wu, Zhuorui Zhang, Qiuyu Zhang, Hepeng Zhang, Molybdenum carbide-promoted cobalt as an efficient catalyst for selective hydrogenation, Ind. Eng. Chem. Res. 59 (32) (2020) 14267–14277.
- [32] Liang Jiang, Peng Zhou, Zehui Zhang, Shiwei Jin, Quan Chi, Synthesis of Secondary amines from one-pot reductive amination with formic acid as the hydrogen donor over an acid-resistant cobalt catalyst, Ind. Eng. Chem. Res. 56 (44) (2017) 12556–12565.
- [33] Tingting Sun, Lianbin Xu, Shengyu Li, Wenxia Chai, Yan Huang, Yushan Yan, Jianfeng Chen, Cobalt-nitrogen-doped ordered macro-/mesoporous carbon for highly efficient oxygen reduction reaction, Appl. Catal. B Environ. 193 (2016) 1–8.
- [34] Ping Yang Di Liu, Hao Zhang, Minjie Liu, Wenfei Zhang, Dongmei Xu, Jun Gao, Direct reductive coupling of nitroarenes and alcohols catalysed by Co-N-C/CNT@ AC, Green Chem. 21 (8) (2019) 2129–2137.
- [35] Wanbing Gong, Yue Lin, Chun Chen, Mohammad Al-Mamun, Hai-Sheng Lu, Guozhong Wang, Haimin Zhang, Huijun Zhao, Nitrogen-doped carbon nanotube confined Co-Nx sites for selective hydrogenation of biomass-derived compounds, Adv. Mater. 31 (2019), 1808341.
- [36] Peng Zhou, Zehui Zhang, One-pot reductive amination of carbonyl compounds with nitro compounds by transfer hydrogenation over Co-N-x as catalyst, ChemsusChem 10 (9) (2017) 1892–1897.
- [37] Ziliang Yuan, Bing Liu, Peng Zhou, Zehui Zhang, Quan Chi, Preparation of nitrogen-doped carbon supported cobalt catalysts and its application in the reductive amination, J. Catal. 370 (2019) 347–356.
- [38] Weijie Geng, Wenxiu Li, Lin Liu, Junhai Liu, Liying Liu, Xiangjin Kong, Facile assembly of Cu-Cu<sub>2</sub>O/N-reduced graphene oxide nanocomposites for efficient synthesis of 2-methylfuran, Fuel 259 (2020), 116267.
- [39] Guoqiang Li, Huanhuan Yang, Haifu Zhang, Zhiyuan Qi, Minda Chen, Wei Hu, Lihong Tian, Renfeng Nie, Wenyu Huang, Encapsulation of nonprecious metal into ordered mesoporous N-doped carbon for efficient quinoline transfer hydrogenation with formic acid, ACS Catal. 8 (9) (2018) 8396–8405.
- [40] Ruixiao Gao, Haotian Guo, Bowei Wang, Pengzhi Qiu, Mingming Sun, Ligong Chen, Co based N, S co-doped carbon hybrids for catalytic hydrogenation: role of cobalt salt and doped S, Appl. Catal. A Gen. 579 (2019) 99–105.
- [41] Xiaohui Sun, Alma I. Olivos-Suarez, Lide Oar-Arteta, Elena Rozhko, Dmitrii Osadchii, Anastasiya Bavykina, Freek Kapteijn, Jorge Gascon, Metalorganic framework mediated cobalt/nitrogen-doped carbon hybrids as efficient and chemoselective catalysts for the hydrogenation of nitroarenes, ChemCatChem 9 (10) (2017) 1854–1862.