



# In Situ Synthesized Silica-Supported Co@N-Doped Carbon as Highly Efficient and Reusable Catalysts for Selective Reduction of Halogenated Nitroaromatics

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Abstract: Silica-supported Co@N-doped carbon (Co@CN/SiO<sub>2</sub>) catalysts were first prepared by a one-step impregnation with a mixed solution of cobalt nitrate, glucose and urea, followed by in situ carbonization and reduction. The Co@CN/SiO2 catalysts were investigated for the selective reduction of nitro aromatics to the corresponding anilines using hydrazine hydrate. The Co@CN/SiO<sub>2</sub>-500 carbonized at 500 °C exhibited the highest catalytic activity and excellent stability without any decay of activity after 6 cycles for the reduction of ntirobenzene. Both metallic Co atoms and Co-N species formed in the Co@CN/SiO<sub>2</sub> catalysts were active, but the Co-N species were dominant active sites. The high activities of the Co@CN/SiO<sub>2</sub> catalysts were attributed to the synergistic effect between the Co and N atoms, promoting heterolytic cleavage of hydrazine to form H<sup>+</sup>/H<sup>-</sup> pairs. Representative examples demonstrated that the Co@CN/SiO<sub>2</sub>-500 could completely transform various halogen-substituted nitro aromatics to the corresponding halogenated anilines with high TOFs and selectivity of > 99.5%.

#### Introduction

Aromatic amines are crucial intermediates for the synthesis of various fine chemicals, such as pharmaceuticals, agrochemicals, dyes, and pigments.<sup>[1,2]</sup> At present, most of aromatic amines are prepared by catalytic reduction of aromatic nitro compounds.<sup>[3,4]</sup> Particularly, heterogeneous catalytic reduction over supported metal catalysts as an environment-friendly and efficient protocol attracts much interest.<sup>[5,6]</sup> Pt-group-metal (Pt, Rh, Ru, Pd) catalysts have been investigated extensively because of their high intrinsic activities for the reduction of nitro aromatics.<sup>[7-9]</sup> Nevertheless, most of these reported noble-metal catalysts are poorly chemoselective for the reduction of nitro aromatics to the corresponding aromatic amines with other reducible functional groups, especially with halogens (F, Cl, Br, I).<sup>[10-12]</sup> Moreover, the scarcity and volatile price of precious metals also limit their large-scale applications in chemical industry.

Supported catalysts based on non-noble metals (Fe, Co, Ni) have been studied to substitute for noble metal catalysts.<sup>[13-17]</sup> The Co-based catalysts attract more attention because they frequently show not only high catalytic activity but also excellent chemoselectivity of aromatic amines for the reduction of various functionalized aromatic nitro compounds.<sup>[18-20]</sup> Nitrogen-doped porous carbon materials have been demonstrated to be excellent catalyst supports for the dispersion of Co species for

the reactions.<sup>[21,22]</sup> N-doping can modify the electronic structures of Co particles and improve the interactions between metal particles and support to form metal-N sites,<sup>[23,24]</sup> which has been reported as highly effective catalytic active sites. For example, CoO<sub>x</sub>@N-doped carbon nanotubes, metal organic frameworks derived Co-based catalysts, and single-atom dispersed Co-N-C catalysts exhibit excellent catalytic properties for the selective reduction of nitroaromatics.<sup>[25-28]</sup> Unfortunately, oxidation and leaching problems of metallic Co active sites are commonly found in the reaction process, which result in deactivation and poor recyclability of the catalysts.<sup>[29-31]</sup> Recently, mesoporous alumina and silica-supported Co nanoparticles and Ni(Co)-MoO<sub>3</sub> catalysts modified with nitrogen-doped graphite-like carbon layers, which were prepared by the two-step impregnation approach using 1,10-phenanthroline as carbon and nitrogen sources, have been reported to be highly efficient for the reduction of nitro aromatics to the corresponding amines with hydrazine hydrate ( $N_2H_4$ · $H_2O$ ), a green hydrogen donor which only produces N<sub>2</sub> and water as by-products in the catalytic reductions.<sup>[32,33]</sup> The catalysts exhibit not only higher catalytic activity than those catalysts supported on carbon materials alone, but also more excellent anti-oxidation ability of metallic Co, remarkably improving the stability and reusability of the catalysts.

Herein, porous silica-supported Co@N-doped carbon materials (Co@CN/SiO<sub>2</sub>) were prepared by a one-step impregnation, followed by in-situ carbonation and reduction at 500 °C. The obtained Co@CN/SiO<sub>2</sub> composites exhibited high catalytic activity as well as excellent chemoselectivity for the selective reduction of various halogenated nitro aromatics to the corresponding haloanilines with hydrazine hydrate. More importantly, there were no oxidation and loss in catalytic performance observed after recycling at least 6 times for the reduction of nitrobenzene, and it was revealed that the Co@CN/SiO<sub>2</sub> by the one-step method had significantly higher stability than the one prepared by the two-step impregnation.

#### **Results and Discussion**

#### **Catalyst characterization**

The real contents of Co, C and N in the prepared materials were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and X-ray photoelectron spectroscopy

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Table 1. Contents of Co, C and N, and specific surface areas, pore volumes and mean pore sizes of the catalysts.

Catalyst	Co (wt%)	C (wt%)	N (wt%)	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Mean pore size (nm)	Co crystallite size by XRD (nm)	Co particle size by TEM (nm)
SiO <sub>2</sub>	_	_	_	324	1.0	12.8	- 7	-
Co <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> -500	13.5	-	-	219	0.68	12.5	-	
Co@C/SiO <sub>2</sub> -500	12.5	19.7	-	245	0.54	10.7	7.0	7.0
CN/SiO <sub>2</sub> -500	_	28.3	7.3	214	0.59	10.9	-	_
Co@CN/SiO2-300	12.2	24.3	11.0	198	0.33	6.7		_
Co@CN/SiO <sub>2</sub> -400	12.1	25.6	8.2	221	0.36	6.4	4.2	4.0
Co@CN/SiO <sub>2</sub> -500	12.4	27.9	6.3	270	0.41	6.3	5.0	4.9
Co@CN/SiO <sub>2</sub> -600	12.3	30.1	5.0	319	0.50	6.2	6.1	5.8
Co@CN/SiO2-700	13.0	22.8	3.2	319	0.49	6.1	6.9	6.8
Co@CN/SiO2-imp-500	12.8	27.5	6.1	221	0.52	9.2	7.1	6.9

(XPS), respectively, and the results are given in Table 1. For the  $Co@CN/SiO_2$ -T (T referred to the carbonization temperature, T = 300, 400, 500, 600, 700) samples, the Co contents were all located at 12.5  $\pm$  0.5 wt%, which were lower than that in the Co<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-500 due to the addition of C and N. However, the calcination temperatures remarkably affected the amounts of C and N incorporated on the catalyst surfaces. The amounts of C components gradually increased with increasing the temperatures for 300 to 600 °C, while the N contents showed a decline trend in the temperature range. These results could be explained by the fact that the C and N organic precursors were progressively condensed on the surfaces, and meanwhile in this process, parts of C-N bonds were cleaved to generate gas Ncontaining compounds, the amounts of which increased with elevating the temperature in the N2 atmosphere. When the temperature was further elevated to 700 °C, the decomposition and gasification of the C-N bonds were sped up, resulting in a rapid decrease in the C and N contents on the catalyst surfaces. In the case of the Co@CN/SiO2-imp-500, there were similar amounts of Co, C and N to the Co@CN/SiO2-500 as summarized in Table 1.

N<sub>2</sub> sorption measurements were applied to analyze the textural properties of the materials. As illustrated in Figure 1a for the SiO<sub>2</sub>, Co@CN/SiO<sub>2</sub>-T (T = 300, 400, 500, 600, 700), CN/SiO<sub>2</sub>-500, and Co@CN/SiO<sub>2</sub>-imp-500 materials, all the samples exhibited typical type IV isotherms with clear hysteresis loops, which were an indication of mesoporous structure, similar to pure silica support. This result demonstrated that the mesoporous structure of silica was still kept after being incorporated with Co, C and N components. The similar pore size distributions of the samples in Figure 1b also proved this point, and the pore sizes were primarily in the range of 5-20 nm. However, as seen in Table 1, all the catalysts showed a remarkable decline in specific surface area, pore volume and pore size due to the incorporation of Co, C and N, compared with pure silica. In the case of the Co@CN/SiO<sub>2</sub>-T(T = 300, 400, 400, 400)500, 600, 700) samples, in general, the specific surface areas and pore volumes gradually increased with increasing the calcination temperature. This result could be attributed to the



Figure 1. (a) N<sub>2</sub> sorption isotherms and (b) BJH pore size distributions of the SiO<sub>2</sub>, CN/SiO<sub>2</sub>-500, Co@CN/SiO<sub>2</sub>-T and Co@CN/SiO<sub>2</sub>-imp-500 catalysts.

condensation and/or decomposition of organic precursors to generate porous amorphous N-containing carbon. The decreases in the pore size with the temperatures were likely due to the formation of more nonporous N-doped graphitic carbon on the pore surfaces, which could be supported by the following XPS spectra in Figure 4. The Co@CN/SiO<sub>2</sub>-imp-500 in Table 1 exhibited slightly smaller specific surface area, but larger pore volume and pore size than the Co@CN/SiO<sub>2</sub>-500, probably because the two-step impregnation route resulted in the blockage of more micropores in the support.

Powder X-ray diffraction (XRD) patterns of the CN/SiO<sub>2</sub>-500, Co@CN/SiO<sub>2</sub>-T (T = 300, 400, 500, 600, 700), and Co@CN/SiO<sub>2</sub>-imp-500 materials are presented in Figure 2. All the samples showed a broad diffraction peak at  $2\theta$  = ~22.5°, which was assigned to amorphous silica and/or graphitic carbon. Because the diffraction patterns of amorphous silica and carbon were overlapped, the carbon structures in the catalysts were analyzed by Raman spectra (not shown). All the Co@CN/SiO<sub>2</sub> catalysts exhibited a defect (D) band at ~1356 cm<sup>-1</sup> and a graphite (G) band at ~1580 cm<sup>-1</sup>, which were attributed to the disordered graphitic carbon and the graphitization degree, respectively.<sup>[19,31]</sup> Generally, the graphitization degrees increased with elevating the calcination temperature. For the

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Figure 2. XRD patterns of the CN/SiO\_2-500, Co@CN/SiO\_2-T and Co@CN/SiO\_2-imp-500 samples.

Co@CN/SiO<sub>2</sub>-T samples, no peak associated with Co species was found for the Co@CN/SiO2-300 sample, indicating that Co oxide species were highly dispersed in the CN/SiO<sub>2</sub> matrix, and that there was no metallic Co particles formed in the calcination process. When the temperature was elevated to 400 °C, a new diffraction peak at  $2\theta = 44.2^{\circ}$  was observed, corresponding to cubic metallic Co (111) reflections (PDF 15-0806). This result indicated that the Co oxides could be reduced to generate metallic Co crystallites with glucose and/or urea under the N2 atmosphere. As the calcination temperature was further increased, the intensity of the diffraction peaks for metallic Co was strengthened, but the peak width became narrower. This result implicated that more Co oxides were reduced to form metallic Co crystallites, and the Co crystallite sizes increased with the calcination temperature. Table 1 gives the mean sizes of the Co crystallites obtained using the peak width of Co (111) by the Scherrer equation. The Co crystallite sizes were enhanced from 4.2 to 6.9 nm when the temperatures were elevated from 400 to 700 °C. As expected, the Co@CN/SiO2imp-500 exhibited stronger diffraction peaks and narrower peak widths for metallic Co than the Co@CN/SiO<sub>2</sub>-500, which was indicative of the reduction of more Co oxides to metallic Co and the presence of larger Co crystallites (7.1 nm). It was noteworthy that the larger Co crystallites (7.0 nm) were also formed on the Co@C/SiO<sub>2</sub>-500 sample in Table 1. This result implied that the use of urea precursor or the addition of N improved the dispersion of metallic Co on the catalyst surface.

Transmission electron microscopy (TEM) images of the  $Co@CN/SiO_2-T$  (T = 300, 400, 500, 600, 700) and  $Co@CN/SiO_2-imp-500$  materials were shown in Figure 3. No metallic Co particles were found on the  $Co@CN/SiO_2-300$ ; however, the  $Co@CN/SiO_2-400$  exhibited sparse darker metallic Co particles with a mean size of ca. 4.0 nm. When the calcination temperatures were continuously increased, both the densities and the average sizes of the Co particles were increased. As seen in Table 1, when the temperature was



Figure 3. TEM images and particle size distributions of the materials. (a) Co@CN/SiO2-300, (b) Co@CN/SiO2-400, (c) Co@CN/SiO2-500, (d) Co@CN/SiO2-600, (e) Co@CN/SiO2-700 and (f) Co@CN/SiO2-imp-500.

elevated from 400 to 700 °C, the Co particle sizes increased from 4.0 to 6.8 nm. In terms of the Co@CN/SiO<sub>2</sub>-imp-500, both the density and the mean size of the Co particles were larger than those for the Co@CN/SiO<sub>2</sub>-500. These results further confirmed that the calcination temperature and preparation route had significant effects on the reduction degree of the Co oxide species with organic precursors, and on the sizes of metallic Co crystallites or particles formed, as revealed by the XRD results in Figure 2 and Table 1. It could be seen from Table 1 that the Co particle sizes counted by TEM were approximately equal to the mean sizes of Co crystallites by XRD. This meant that the Co particles existed in the single crystalline form, which was also proved by the typical HR-TEM images of Co particles (not shown).

The XPS spectra were used to study the elemental compositions, chemical states and the interactions among the elements on the surfaces. The analysis of the XPS survey spectra revealed that for all the Co-containing catalysts in Table 2, the surface Co compositions were much lower than those determined by ICP in Table 1. This result demonstrated that the Co species might be situated mainly below the surface and subsurface of the matrices. In the case of the Co@CN/SiO<sub>2</sub>-*T*(*T* = 300, 400, 500, 600, 700), the Co contents on the surfaces

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Table 2. Total Co contents and Co compositions in individual Co specie	es on
the catalyst surface by XPS.	

Catalyst	Total surface Co (wt%)	Metallic Co (wt%)	Co <sub>3</sub> O <sub>4</sub> (wt%)	Co–N (wt%)
Co <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> -500	6.3	0	6.3	0
Co@CN/SiO2-300	5.9	0	4.8	1.1
Co@CN/SiO2-400	5.4	0.5	3.7	1.2
Co@CN/SiO2-500	4.8	1.3	1.3	2.2
Co@CN/SiO2-600	3.5	1.5	0.9	1.1
Co@CN/SiO2-700	2.2	1.2	0.5	0.5
Co@CN/SiO2-imp-500	2.8	1.6	0.7	0.5

decreased with elevating the calcination temperature mainly because of the combination of two factors of the increases in C contents and particle sizes of metallic Co on the catalyst surfaces. Furthermore and for the same reason, the surface Co composition on the Co@CN/SiO<sub>2</sub>-500 was higher than on the Co@CN/SiO<sub>2</sub>-imp-500, but smaller than on the Co<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-500 as shown in Table 2.

Figure 4a displays the Co 2p XPS spectra of the Co<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-500,  $Co@CN/SiO_2-T$  (T = 300, 400, 500, 600, 700) and Co@CN/SiO2-imp-500 samples. It could be found that the Co<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-500 sample exhibited a symmetric Co 2p<sub>3/2</sub> primary spectrum peaked at the binding energy (BE) of 780.7 eV, which was assigned to Co<sub>3</sub>O<sub>4</sub>.<sup>[34,35]</sup> For the Co@CN/SiO<sub>2</sub>-T samples, a broadened non-symmetric Co 2p<sub>3/2</sub> peak was observed, which could be deconvoluted into two or three components. The Co@CN/SiO<sub>2</sub>-300 had two peaks positioned at the BEs of 780.7 eV and 782.5 eV, corresponding to  $Co_3O_4$  and Co-N species, respectively.<sup>[23,24,26,36]</sup> When the calcination temperature was increased to 400  $^{\circ}\text{C},$  a new peak at the BE value of 778.2 eV appeared for metallic Co,<sup>[26,37]</sup> and its peak intensity was strengthened with the increase in the temperature relative to the total Co species. These results demonstrated that Co oxides could be reduced to metallic Co above 400 °C, and the relative amounts of metallic Co were enhanced with the temperature (Table S1), which was in agreement with the XRD and TEM results shown in Figure 2 and Figure 3. In terms of the Co-N species formed on the surfaces, the relative peak intensity to total Co species increased with elevating the calcination temperature, but exhibited a maximum at 500 °C (Table S1). This phenomenon could be attributed to the formation of larger Co particles and the reduction in N content on the catalyst surfaces at higher temperatures as listed in Table 1. The Co percentage contents in the individual Co species on the catalyst surfaces were calculated and summarized in Table 2. It could be seen that for the Co@CN/SiO<sub>2</sub>-T catalysts, the Co<sub>3</sub>O<sub>4</sub> contents on the surfaces always decreased with the calcination temperature, however, the content of metallic Co for the Co@CN/SiO<sub>2</sub>-600 and the Co content in the Co-N species for the Co@CN/SiO<sub>2</sub>-500 showed a maximum value, respectively, due to the combination factors including total Co contents, Co particle sizes and N contents on the catalyst surfaces. As for the Co@CN/SiO<sub>2</sub>-imp-500, more Co oxide was reduced into metallic Co, but significantly smaller amounts of Co-N species were formed, compared with the Co@CN/SiO<sub>2</sub>-500.

The N 1s XPS spectra of the prepared catalysts are illustrated in Figure 4b. The N 1s XPS spectra of the Co@CN/SiO<sub>2</sub>-T (T =300, 400, 500) could be fitted into two components peaked at the BEs of 398.5 eV and 399.5 eV, which were attributed to pyridine-type N, pyridinic N for the Co-N species and/or pyrroletype N, respectively.<sup>[38-41]</sup> When the temperature was elevated to 600 °C, graphitic N was observed at the BE of 401.0 eV,<sup>[42,43]</sup> and its relative peak intensity was strengthened with further increasing the temperature, and in the meanwhile, the relative peak intensity for pyridinic N was found to be decreased. However, the peak intensities for the pyridinic N for the Co-N and/or pyrrole-type N showed no obvious change (Table S2). These results also suggested that graphitic N atoms should be formed predominantly by the transformation of the pyridinic N atoms in the matrices. It was noteworthy that the CN/SiO<sub>2</sub>-500 exhibited a clear N 1s XPS spectrum from graphitic N, but a weaker relative intensity of pyridinic N compared with the  $Co@CN/SiO_2-T$  (T = 300, 400, 500). This result indicated that the presence of Co could suppress the transformation of pyridinic N to graphitic N probably by the formation of Co-N during the pyrolysis process of organic precursors. In terms of the Co@CN/SiO2-imp-500, more pyridinic N atoms were transformed into graphitic N atoms, compared with the Co@CN/SiO2-500.



Figure 4. XPS spectra of the Co<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-500, Co@CN/SiO<sub>2</sub>-T, Co@CN/SiO<sub>2</sub>imp-500, and CN/SiO<sub>2</sub>-500 samples.

It has been reported that the pyrrolic and pyridinic N sites not only provide strong N coordination but also act as anchoring sites for the formation and stabilization of Co particles.<sup>[44,45]</sup> The Co@CN/SiO<sub>2</sub>-500 and Co@CN/SiO<sub>2</sub>-imp-500 samples were analyzed by XPS after exposure to air for more than 3 months (Figure S1). It was found that the Co 2p spectra of the Co@CN/SiO<sub>2</sub>-500 exhibited no change, while that of the Co@CN/SiO<sub>2</sub>-imp-500 demonstrated that all of metallic Co was re-oxidized on the surface. This result revealed that the Co@CN/SiO<sub>2</sub>-500 catalyst possessed superior anti-oxidation ability in air.

#### **Catalytic reaction**

Nitrobenzene was first applied as a model compound to compare the catalytic activities over the prepared catalysts for the selective reduction of nitro aromatics to the corresponding anilines with hydrazine hydrate and the reaction results are summarized in Table 3. The CN/SiO<sub>2</sub>-500 and Co<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-500 catalysts (entries 1 and 2) showed no activity, while the fresh Co<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-500-H<sub>2</sub> obtained by the H<sub>2</sub> reduction at 500 °C without exposure to air exhibited a 3.0% nitrobenzene conversion under the identical conditions (entry 3). However, when the Co<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-500-H<sub>2</sub> was exposed to ambient air for more than 24 h, it became almost completely deactivated due to the surface oxidization of metallic Co. These results demonstrated that metallic Co atoms on the surfaces were active to a certain extent. All the Co@CN/SiO2-T and Co@CN/SiO<sub>2</sub>-imp-500 catalysts (entries 4–9) exhibited significantly higher conversions of nitrobenzene. This result implicated that the presence of N-doped carbon from glucose and urea precursors could greatly improve the performance of the Co@CN/SiO<sub>2</sub> catalysts for the selective reduction of nitro aromatics with hydrazine.

The reaction results in entries 4-8 of Table 3 revealed that the calcination temperatures significantly affected the activity of the  $Co@CN/SiO_2$ -T for the selective reduction of nitrobenzene. The nitrobenzene conversions increased with elevating the temperature, and showed a maximum value of 65.3% at 500 °C. Turnover frequency (TOF) estimated on the basis on the total moles of Co in the Co@CN/SiO<sub>2</sub>-500 by ICP reached 4282 h<sup>-1</sup> (Table 4), which, to the best of our knowledge, was the highest TOF over various non-noble metal and metal-free catalysts ever reported for the selective reduction of nitrobenzene with hydrazine,<sup>[46]</sup> sodium borohydride,<sup>[47]</sup> formic acid<sup>[48]</sup> or gas hydrogen<sup>[49]</sup> as a reducing agent under similar reaction conditions (Table S3). When the temperature was further elevated, the nitrobenzene conversion showed a clear decline, for instance, 20.3% and 14.7% for Co@CN/SiO<sub>2</sub>-600 and Co@CN/SiO<sub>2</sub>-700, respectively. These variations matched well with the compositions of Co-N species on the catalyst surfaces shown in Table 2. It could be concluded that the Co atoms with the strong interaction with the N atoms, i.e., Co-N species, were dominantly responsible for the high catalytic activity of the  $Co@CN/SiO_2-T$  catalysts. However, the nitrobenzene conversion was only 3.5% even at 120 °C for the Co@CN/SiO2-500 catalyst with hydrogen as the reducing agent. This phenomenon implied that the nitrobenzene reduction was not performed through the decomposition hydrogenation route, although hydrazine was easy to be decomposed into N2 and H<sub>2</sub>.<sup>[50,51]</sup> The Co@CN/SiO<sub>2</sub>-imp-500 only showed a lower

<b>Table 3.</b> Selective reduction of nitrobenzene to aniline over various catalysts <sup>[a]</sup> .					
Entry	Catalyst	Conv. (%)	Sel. (%)		
1	CN/SiO <sub>2</sub> -500	0	-		
2	Co <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> -500	0.1	100		
3	Co <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> -500-H <sub>2</sub>	3.0	100		
4	Co@CN/SiO <sub>2</sub> -300	32.1	100		
5	Co@CN/SiO <sub>2</sub> -400	41.2	100		
6	Co@CN/SiO <sub>2</sub> -500	65.3	100		
7	Co@CN/SiO <sub>2</sub> -600	20.3	100		
8	Co@CN/SiO <sub>2</sub> -700	14.7	100		
9 <sup>b</sup>	Co@CN/SiO <sub>2</sub> -500	3.5	100		
10	Co@CN/SiO <sub>2</sub> -imp-500	12.0	100		
11	Fe@CN/SiO <sub>2</sub> -500	5.0	100		
12	Ni@CN/SiO <sub>2</sub> -500	9.5	100		
13	Pt@CN/SiO <sub>2</sub> -500	33.4	100		
14	Pd@CN/SiO <sub>2</sub> -500	20.8	100		

[a] Reaction conditions: 150 mmol nitrobenzene, 25 mg catalyst, 20 mL ethanol, 600 mmol N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, 70 °C, 30 min. [b] Reaction conditions: 150 mmol nitrobenzene, 25 mg catalyst, 20 mL ethanol, 2.0 MPa H<sub>2</sub>, 120 °C.

nitrobenzene conversion of 12.0% (entry 10), due to smaller amounts of Co–N active species on the catalyst surface as shown in Table 2, compared with the Co@CN/SiO<sub>2</sub>-500. Entries 11–14 in Table 3 also demonstrated that the catalytic activity of the Co@CN/SiO<sub>2</sub>-500 for the reduction of nitrobenzene was not only higher than non-noble metal Fe, Ni@CN/SiO<sub>2</sub>-500, but also more excellent than noble metal Pt, Pd@CN/SiO<sub>2</sub>-500 catalysts by the same one-step impregnation method. In Table 3, all the catalysts exhibited an aniline selectivity of 100% for the selective reduction of nitrobenzene.

The reduction of nitrobenzene was further used to investigate the stability and recyclability of the Co@CN/SiO<sub>2</sub>-500 and Co@CN/SiO<sub>2</sub>-imp-500 for comparison. The reaction conditions for ca. 88.3% nitrobenzene conversion at 60 min over the Co@CN/SiO<sub>2</sub>-500 were selected for the first reaction, where the reduction of nitro groups was controlled by chemical kinetics. The spent catalyst after every reaction was recovered by centrifugation, washing with ethanol and drying at 80 °C. As presented in Figure 5, the nitrobenzene conversions were almost kept constant over the Co@CN/SiO<sub>2</sub>-500 for the 6-time cycles. In contrast, the nitrobenzene conversions over the Co@CN/SiO<sub>2</sub>-imp-500 declined from 20.4% for the first reaction to 13.1% after 6 cycles. After every cycling reaction, the Co contents in the product solutions were determined by ICP-AES. The solutions for the Co@CN/SiO<sub>2</sub>-500 hardly contained the Co element (< 1 ppm), while for the Co@CN/SiO<sub>2</sub>-imp-500, the Co contents in the solutions were always above 20 ppm.

The spent catalysts were characterized by XRD, TEM, XPS, and ICP. It could be found that XRD patterns and TEM images of the spent  $Co@CN/SiO_2$ -500 and  $Co@CN/SiO_2$ -imp-500 catalysts had no observable variations in phase structure and Co particle size after 6 cycles (Figure S2 and S3). Figure 6 also

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revealed that the Co@CN/SiO<sub>2</sub>-500 before and after cycling exhibited almost the same XPS Co 2p spectra; however, for the spent Co@CN/SiO<sub>2</sub>-imp-500, the peak for metallic Co disappeared after the cycles, indicating that the metallic Co atoms on the surface were re-oxidized into Co oxides. These results further confirmed that the Co@CN/SiO<sub>2</sub> catalysts by our one-step impregnation and in-situ carbonization method had more excellent anti-oxidation ability for the reactions. ICP analysis demonstrated that the total Co content in the spent Co@CN/SiO<sub>2</sub>-500 was 12.1%, very close to that before the reaction in Table 1; and the Co content of the spent Co@CN/SiO<sub>2</sub>-500-imp was 8.5 wt%, obviously lower than that before the reaction.

The halogenated anilines were an important group of key intermediates and raw materials in the pharmaceutical industry, such as chlorfluazuron and hexaflumuron.<sup>[52-54]</sup> However, over traditional noble metal catalysts the selective reduction of the halogenated nitro aromatics to the halogenated anilines always made some unwanted dehalogenated side-products which are difficult to separate, seriously reducing the product quality.<sup>[55-57]</sup>



Figure 5. Reuse tests of the  $Co@CN/SiO_2$ -500 and  $Co@CN/SiO_2$ -imp catalysts. Reaction conditions: 150 mmol nitrobenzene, 25 mg catalyst, 600 mmol N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, 20 mL ethanol, 70 °C, 60 min.



The reductions of some representative halogen-substituted nitro aromatics were examined over the Co@CN/SiO<sub>2</sub>-500 catalyst using hydrazine hydrate and the results are given in Table 4. To our great surprise, all the halogenated nitro aromatics could smoothly be transformed into the corresponding halogenated anilines with a selectivity of > 99.5%. The halogen atoms on benzene rings exhibited a great and complicated influence on the catalytic activity. However as a whole, the catalytic activity for the reduction of the halogen-substituted nitro aromatics with a halogen atom at the same position could be found to follow the following order: Br > I > Cl > F (entries 2-11), which was different from that on Pt-based catalysts (F > Cl > Br > I) reported in the previous document;<sup>[51,58]</sup> This phenomenon meant that the reductions of the halogenated nitro aromatics over the Co@CN/SiO<sub>2</sub> catalysts might have different reaction mechanism from those over the Pt-based catalysts. For the reduction of the halogen-substituted nitro aromatics with the same halogen atom at the different positions, the catalytic activity followed the order: ortho- > meta- > para-. Entries 21 and 22 in Table 4 revealed that the halogenated N-heterocyclic nitro aromatics could also be smoothly and quantitatively converted to the corresponding halogenated N-heterocyclic aromatic amines with high TOFs.

Table 4. Selective reducitons of various halogenated nitroarenes over  $Co@CN/SiO_{2}-500^{[a]}$ .

Entry	Substrate	Time (min)	Conv. (%)	Sel. (%)	TOF <sup>[b]</sup> (h <sup>-1</sup> )
1		70	100	>99.5	4282
2	F-NO2	480	100	>99.5	552
3		240	100	>99.5	971
4	Br-NO <sub>2</sub>	150	100	>99.5	1959
5		180	100	>99.5	1266
6	CI NO2	180	100	>99.5	1239
7	Br NO <sub>2</sub>	150	100	>99.5	2267
8	NO <sub>2</sub>	150	100	>99.5	2062
9		180	100	>99.5	1371
10	NO <sub>2</sub> Br	100	100	>99.5	3547
11	NO <sub>2</sub>	120	100	>99.5	2501

NO

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12	CI CI	70	100	>99.5	4162
13	F NO <sub>2</sub> Br	70	100	>99.5	4052
14	CI NO <sub>2</sub> Br	100	100	>99.5	3437
15	Br NO <sub>2</sub>	100	100	>99.5	3547
16		100	100	>99.5	3405
17	CI NO <sub>2</sub>	190	100	>99.5	1246
18	CI NO2	150	100	>99.5	2343
19	CI NO <sub>2</sub> NH <sub>2</sub>	80	100	>99.5	3851
20	CI NO <sub>2</sub> CI NH <sub>2</sub>	80	100	>99.5	3741
21		100	100	>99.5	3362
22		150	100	>99.5	1869

[a] Reaction conditions: 30 mmol substrate, 5 mg catalyst, 4 mL ethanol, 120 mmol N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, 70 °C. [b] Based on total metal by ICP and initial substrate conversions at 10 min.

# Reduction mechanism of nitro aromatics over $Co@CN/SiO_2$ catalysts

It is widely believed that the reduction of nitro aromatics to the corresponding aniline proceeds by the two reaction pathways, i.e., direct and indirect. The direct way includes two consecutive steps of nitro group to the nitroso, and then to the hydroxylamine, and finally the hydroxylamine is reduced into the amine; whereas the indirect way involves the azo intermediates condensed bv the nitroso and hydroxylamine intermediates.<sup>[38,59,60]</sup> For the reduction of nitrobenzene as the model reaction over the Co@CN/SiO2 catalysts, no intermediates including nitrosobenzene, phenylhydroxylamine and azoxybenzene were detected in the product solutions. In order to make clear the reaction routes of nitro aromatics with hydrazine hydrate, some separate experiments were designed over the Co@CN/SiO<sub>2</sub>-500. It was found that the reduction rate of phenylhydroxylamine to aniline was significantly faster than that of nitrobenzene with hydrazine; while the reduction of azoxybenzene could hardly proceed under the identical reaction conditions. These results clearly demonstrated that the reduction of nitro aromatics to the corresponding anilines was performed over the Co@CN/SiO<sub>2</sub> catalysts through the direct route.

Metal nitrides have widely been studied and exhibited excellent catalytic performance for hydrazine decomposition to  $H_2$  and  $N_2$ .<sup>[61-63]</sup> It could be assumed that the dissociation of hydrazine on the surface Co-N species of the Co@CN/SiO2 catalysts was also performed through the similar mechanism of hydrazine to on metal nitride for the selective reduction of nitro groups. Therefore, it was proposed that hydrazine molecule might be first adsorbed on the metallic Co atoms; the synergistic effect between the Co and pyridinic N atoms in the Co-N species promoted heterolytic cleavage of hydrazine hydrate to form H<sup>-</sup> species and split-over H<sup>+</sup> species in a Co-H<sup>-</sup> form and in a N-H<sup>+</sup>, respectively.<sup>[50,64,65]</sup> The nitro groups on the catalyst surface interacted with the adjacent H<sup>+</sup>/H<sup>-</sup> pairs to form the nitroso intermediates. These nitroso compounds were further reduced to hydroxylamine, which was directly hydrogenated to benzene amine (Scheme 1).

Besides, our experiments demonstrated that the fresh Co<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-500-H<sub>2</sub> showed no activity and the Co@CN/SiO<sub>2</sub>-500 generated small amounts of benzene for the reaction of chlorobenzene alone in ethanol with hydrazine hydrate; however, ethanol solution of mixed chlorobenzene and for the nitrobenzene, the Co@CN/SiO2-500 was completely deactivated for the dechlorination of chlorobenzene, but still remained almost unchanged activity for the reduction of nitrobenzene. This result indicated that nitro and CI groups should be competitively adsorbed on the catalyst surface for the reactions. It was concluded that the high selectivity for the selective halogenated nitro aromatics over the Co@CN/SiO<sub>2</sub> could be attributed to the following aspects: 1) lower activity of the catalyst itself for the dehalogenation of halogenated nitro aromatics; 2) competitive adsorption of nitro groups on the catalyst surface inhibiting the dehalogenation of halogenated nitro aromatics.



Scheme 1. Possible reduction mechanism of nitroarenes with hydrazine.

### Conclusion

Silica-supported Co@N-doped carbon catalysts (Co@CN/SiO<sub>2</sub>) have been developed by the one-step impregnation and in situ carbonization. The Co@CN/SiO<sub>2</sub> catalysts could completely transform various halogen-substituted nitro aromatics to the corresponding aromatic amines with a TOF of 4282 h<sup>-1</sup> and a selectivity of > 99.5% with hydrazine hydrate. The Co–N species formed in the Co@CN/SiO<sub>2</sub> catalysts were dominant active sites for the reduction of nitro aromatics. The synergistic effect

between the Co and N atoms promoted heterolytic cleavage of hydrazine hydrate to form H<sup>+</sup>/H<sup>-</sup> pairs, resulted in higher activity of the Co@CN/SiO<sub>2</sub> catalysts. The recycling tests indicated that the Co@CN/SiO<sub>2</sub>-500 catalyst was highly stable and could be reusability for the selective reduction of nitroarenes without any loss of catalytic performance and leaching of metal components due to its high anti-oxidation ability. The present study can be extended to design other transition metal-based catalysts for various catalytic reactions.

### **Experimental Section**

#### Chemicals

Commercial SiO<sub>2</sub> was purchased from Huating (Shanghai) Nano Science & technology Co., Ltd. The SiO<sub>2</sub> powder was washed and calcined at 550 °C for 6 h before being used as the support. Glucose, urea, metal salts, hydrazine hydrate aqueous solution (80 wt%) and all nitro compounds were bought from Sinopharm Chemical Reagent Co., Ltd. All chemicals and solvents were used as received without further treatment. The gases  $(H_2, N_2)$  used for catalyst preparation and reaction were ultra-highly pure.

#### **Catalyst preparation**

The Co/CN@SiO<sub>2</sub> catalysts were prepared by a facile one-step impregnation method, followed by in situ carbonization and reduction in a flow of N<sub>2</sub>. In a typical process, 1 g of commercial SiO<sub>2</sub> powder was added into a mixed aqueous solution of 20 mL containing 1 g of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 0.5 g of glucose, and 1.5 g of urea at room temperature under stirring for 2 h. Then, the mixture was evaporated under stirring at 60 °C. The obtained solid was calcined in a flow of high-purity N<sub>2</sub> (30 mL min<sup>-1</sup>) at 300–700 °C for 1 h at a heating rate of 2 °C min<sup>-1</sup>. The obtained catalyst was denoted as Co@CN/SiO<sub>2</sub>-*T* (*T* referred to the carbonization temperature).

For comparison, CN/SiO<sub>2</sub>-500, Co@C/SiO<sub>2</sub>-500, Fe@CN/SiO<sub>2</sub>-500, and Ni@CN/SiO<sub>2</sub>-500 were prepared by the identical one-step route with the aqueous solutions containing the same mass percentages of metal and/or carbon and nitrogen sources; Pt@CN/SiO<sub>2</sub>-500, and Pd@CN/SiO2-500 containing 2 wt% noble metals were also prepared by the same approach, except that H<sub>2</sub>PtCl<sub>6</sub> and PdCl<sub>2</sub> were used as Pt and Pd sources, respectively; The Co<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-500 was prepared by the same way as the Co/CN@SiO<sub>2</sub>-500 with the Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O aqueous solutions without carbon and nitrogen sources. The Co<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-500-H<sub>2</sub> was obtained by reduction of the Co<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-500 at 500 °C for 2 h in a 30 vol% H<sub>2</sub>/N<sub>2</sub> flow. The Co@CN/SiO<sub>2</sub>-imp-500 catalyst was prepared by a two-step impregnation approach. Namely, the CN/SiO<sub>2</sub>-500 was first obtained, then the CN/SiO2-500 powder was impregnated with an aqueous solution of  $Co(NO_3)_2 \cdot 6H_2O$ , and finally the mixture was evaporated at 60 °C and calcined at 500 °C in a tubular furnace in a flow of high-purity  $N_2$  (30 mL min<sup>-1</sup>) for 1 h.

#### Catalyst characterization

XRD patterns were recorded with a Bruker D8 Advance diffractometer using Cu K $\alpha$  radiation ( $\lambda$  = 0.1542 nm) operated at a voltage of 40 kV and a current of 40 mA. XPS information was analyzed on an ESCALAB 250Xi spectrometer equipped with monochromatized Al K $\alpha$  radiation (hv = 1486.6 eV) operated at ca. 1 × 10<sup>-9</sup> Torr. The spectra were calibrated using the binding energy of C 1s peak at 284.6 eV. The contents of C and N elements in the samples were obtained by XPS. The amounts of metals in the catalysts were analyzed by ICP-AES conducted on a Perkin Elmer emission spectrometer. The N<sub>2</sub> adsorption-desorption isotherms were obtained on a Micromeritics ASAP 2020 analyzer. Before measurement, the samples were degassed at 200 °C for 8 h. The

specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method and the single-point pore volume was calculated from the amount of nitrogen adsorbed at a relative pressure of 0.990. The mean pore sizes were obtained by the BJH method. The pore size distributions were calculated using the adsorption branches of the N<sub>2</sub> sorption isotherms by the Barrett–Joyner–Halenda (BJH) method. Raman measurements were carried out at room temperature on a Renishaw 2000 Ramascope with an Ar<sup>+</sup> ion laser (514.4 nm) as the excitation source. Prior to each measurement, the spectrometer was calibrated with a silicon wafer. TEM analysis was performed on a JEOL JEM-2010F field emission microscope at an acceleration voltage of 200 kV. The samples were prepared by drying an ethanolic dispersion of the well-ground catalyst powder on a holey-carbon-coated copper grid.

#### Catalytic reaction and product analyses

The chemoselective reduction of aromatic nitro compounds was carried out in a two-necked flask of 200 mL with a water-cooled condenser tube, which was placed in a thermostatic water bath with a magnetic stirrer. In a typical experiment, 150 mmol of nitro aromatics, 25 mg catalyst, 20 mL of ethanol, and 1 mL of n-decane as an internal standard were added into the flask, and kept stable at 70 °C for 30 min. Then 600 mmol of hydrazine hydrate was rapidly added into the reaction solution under vigorous stirring at a stirring rate of 800 rpm. After the reaction, the liquid solution was separated from the reaction mixture by centrifugation or magnet for analysis. Each reaction was repeated more than three times to reach the carbon balance of more than 98%. The solutions were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The qualitative and quantitative analyses of the products were done by gas chromatography-mass spectrometry (GC-MS) (Shimadzu GCMS-QP 2010 Plus), and GC (Varian CP-3800) with a capillary column (column HP-5, 30 m length, 0.32 mm internal diameter, 0.25 µm film thickness) and a flame ionization detector, respectively.

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**Keywords:** Heterogeneous catalysis • Halogenated nitroarenes • Chemoselective reduction • N-doped carbon • Co nanoparticles

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The Co@CN/SiO<sub>2</sub> catalysts prepared by a one-step impregnation route exhibit high catalytic activity and excellent stability for the reduction of nitro aromatics with hydrazine hydrate. Representative examples demonstrate that the Co@CN/SiO<sub>2</sub> catalysts can completely transform various halogen-substituted nitro aromatics to the corresponding halogenated anilines with high TOFs and selectivity of > 99.5%.