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Cobalt in N-Doped Carbon Matrix Catalyst for

Chemoselective Hydrogenation of Nitroarenes

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Graphical abstract



Highlights:

- High moiety-tolerance ability and reuse stability can be obtained on Co/NC catalyst.
- Co/NC catalyst has composite structure of $Co@Co_3O_4\&CoN_x$ and N-doped C layers.

- H₂-D₂ exchange results suggest that fast H₂ dissociation enhance the hydrogenation activity.
- Reactant adsorption tests indicate that facile adsorption promotes the hydrogenation reaction.

Abstract:

Anilines as important intermediates for both organic synthesis and industrial manufactory are densely substituted with a variety of functional moieties, and the transformation of nitroarenes into corresponding anilines requires catalytically selective hydrogenation catalyst. Herein, we describe a simple pyrolysis strategy to prepare cobalt catalysts in nitrogen-doped carbon matrix applied in the selective hydrogenation of nitroarenes with molecular hydrogen. The Co/NC catalysts are obtained through thermal treatment of mixed precursors of cobalt phthalocyanine and melamine. The surface-modified Co particles with Co₃O₄ and CoN_x sites are surrounded by N-doped carbon layers according to a series of structural characterization results. These Co/NC catalysts are capable of efficiently selective hydrogenation of nitrobenzene and various substituted nitroarenes into corresponding anilines under relatively mild reaction conditions. The optimal catalytic hydrogenation performance is contributed to the fast rate of H₂ dissociated activation on the CoN_x active sites and the facile adsorption of the reactant substances, which is verified by the isotopic H₂-D₂ exchange experiments, reactant adsorption and the ORR reaction tests.

Furthermore, the heterogeneous Co/NC catalyst is highly stable without the Co leaching and deactivation issues during the recycling reaction runs.

Keywords:

nitroarenes, anilines, selective hydrogenation, cobalt catalyst, N-doping carbon

1. Introduction

The reduction of nitroarenes to their substituted anilines is of great significance in organic synthesis and industrial production of a variety of high-value intermediates including dyes, pharmaceuticals and agrochemicals [1-3]. Functional anilines can be obtained by using stoichiometric reducing agents, e.g., Na₂S₂O₄ [4,5], N₂H₄ [6,7], NaBH₄ [8,9] and NH₃BH₃ [10,11], nonetheless, these reduction processes lead to serious environmental pollution issues. Molecular hydrogen is thus a more attractive and cleaner reductant, and accordingly the catalytic hydrogenation using hydrogen is of great interests for both academic research and industrial productions [12-14]. Heterogeneous catalysts containing supported noble metal nanoparticles (NPs) are industrially employed in the direct hydrogenation of nitroarenes [15-19]. Considering the fact that several valuable anilines are densely substituted with easily reduced or eliminated functional groups, especially ketones, aldehydes, alkenes, alkynes or halogens, a high catalytic chemoselectivity is essential for an ideal applicable hydrogenation catalyst. The superiority of the selective catalyst in the context of moiety-tolerance will allow us to replace the complicated multi-step synthesis involving group-protecting, separation and purification processes [20]. The modification of certain additives on the Pt catalyst has demonstrated to be one of effective one-step solutions for nitroarenes hydrogenation reaction [21]. Corma's group has also reported excellent Au-based catalysts to achieve highly selective hydrogenation of nitro group in the presence of a number of reducible substituent groups [22]. Nonetheless, the practical nitroarenes hydrogenation processes are still

suffering the chemoselectivity issue and the promising catalyst has to be less expensive, highly active without compromising selectivity.

In addition to the noble metal catalysts, tremendous efforts have attempted to develop cost-effective hydrogenation catalysts based on first-row transition metals [23-26]. Beller's group has reported the nanoscale cobalt oxides-based catalysts that were capable of highly selective hydrogenation of nitro group for more than 80 nitroarenes [27-30]. The catalysts were composed of the active cobalt oxide particles surrounded by a nitrogen-doped carbon layer, and such unique structure can be furnished by a pyrolytic deposition of metal-phenanthroline complexes on carbon support. Although these Co catalysts supported on N-doped carbon sheets displayed the superior selectivity towards hydrogenation of nitro group, some debate upon the structure and the catalytic effects Co-relevant active sites still remains: (i) metallic Co⁰ or oxidized CoO_x, (ii) accessible or inaccessible Co sites, and (iii) catalytic mechanism of active coN_x species. Hence, to better rationalize the relation between the catalytic activity and the status of Co sites in Co-catalyzed nitroarene hydrogenation reactions, precise synthesis method to gain well-controlled structure should be further explored.

Controllable pyrolysis can afford the selective metal/NC catalysts by employing different metal salts (i.e. acetate, nitrate, etc.), nitrogen precursors (i.e. urea, melamine, 1,10-phenanthroline, etc.) and structure directing agents in certain processing steps [31-38]. A variety of carbon materials have been also employed as the catalyst supports, including active carbon (AC), carbon nanotubes (CNTs) and carbon black (CB) [39,40]. Another proven synthesis strategy is the carbonization of metal-organic-frameworks

(MOFs) consisting of both metals and N species under high-temperature [10,23,41-44]. Delicate modification on the MOFs can optimize the homogeneous dispersion of metal sites and porous structure. For instance, the specific coordination interaction provided by the amine groups at the MOFs skeleton assists the formation of isolated single-atom Ru sites supported on N-doped porous carbon [45].

Herein, we report a simple method to synthesize Co/NC catalysts via the pyrolysis of the mixture of cobalt phthalocyanine and melamine with different molar ratios. The structure of Co-relevant sites in N-doped carbon matrix is carefully investigated with various characterizations. The Co/NC catalysts are further applied on the chemoselective hydrogenation of nitroarenes to their substituted anilines, and their catalytic activity and selectivity as well as reusability are evaluated under a relatively mild condition. We also study the H₂ dissociation and reactant adsorption on active Co sites to understand the catalytic effects of the Co/NC catalysts.

2. Experimental

2.1. Materials

Melamine (99%) was obtained from Aladdin Reagent Corp. (Shanghai, China). Cobalt phthalocyanine (CoPc, 99%), nitrobenzene (99.5%), aniline (99.9%), and a series of derivatives were purchased from Sigma-Aldrich (Shanghai, China). The nitroarenes includes 2-chloro-1-fluoro-4-nitrobenzene (98%), 1,3,5-trichloro-2nitrobenzene (95%), 1,2-dichloro-4-fluoro-5-nitrobenzene (95%), 1-bromo-4,5dimethoxy-2-nitrobenzene (99%), 4-nitrobenzonitrile (97%), 1-doto-3-nitrobenzene (99%), 2-nitro-4-(trifluoromethyl)benzaldehyde (99%), 4-nitrobenzaldehyde (98%), 2-

nitro-4-(trifluoromethyl)benzonitrile (97%), 1,3,5-trimethyl-2-nitrobenzene (97%), 1nitronaphthalene (97%). N₂ (99.999%), H₂ (99.999%) and He (99.999%) were supplied by Nanjing Special Gas Factory (Nanjing, China). Pure D₂ (99.999%, deuteration degree >99.8%) was purchased from Suzhou Changyou Gas Co., Ltd. (Suzhou, China).

2.2. Catalyst preparation

A certain amount (0.15-0.45 g) of CoPc and 5 g of melamine were thoroughly milled and the formed blue powder was transferred to a crucible. The first-stage pyrolysis procedure was performed in a muffle furnace at 300 °C for 1 h and then at 550 °C for 2 h with a heating rate of 2 °C/min. After natural cooling to room temperature, the resulting solid was fully ground. The second-stage pyrolysis was performed in a tubular furnace at 900 °C for 2 h with a heating rate of 3 °C/min in 50 mL/min of N₂. The powder sample was finally obtained after cooling, which was named after Co/NC-x (x=0.15 to 0.45 depending on the adding amount of CoPc precursor). The reference sample 'NC' was also prepared through same procedure without mixing CoPc.

2.3. Catalyst characterization

The Co contents in the catalysts were measured by inductively coupled plasma optical emission spectrometry (ICP-OES, Avio 200, PerkinElmer). Powder X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Advance diffractometer using Cu K α radiation (λ =0.154 nm) at 40 kV and 40 mA. The N₂ adsorption-desorption measurements were performed at 77 K on a Quantachrome Autosorb-iQ3 adsorption apparatus to obtain the Brunauer-Emmett-Teller (BET) specific surface areas. Prior to measurement, the sample was degassed under vacuum at 473 K overnight.

Transmission electron microscopy (TEM) was performed by using a JEOL 2100F instrument operating at 200 kV. X-ray photoelectron spectra (XPS) were recorded on a VG Scientific ESCALAB Mark II spectrometer. All binding energies were referenced to the peak of C 1s core level at 284.6 eV. The Raman measurements were carried out on a Horiba HR Evolution spectrometer with 532 nm excitation laser.

2.4. Catalytic hydrogenation of nitroarenes

The catalytic hydrogenation reaction of nitroarenes was carried out in a 50 mL Hastelloy batch reactor with a Teflon liner (NS-50-C276, Anhui Kemi Machinery Technology Co., Ltd.). Catalyst (30 mg), nitrobenzene or functionalized nitroarenes (2 mmol), and ethanol solvent (10 mL) were added into the reactor. The residual air in the reactor was removed by pressurizing and releasing H₂ gas several times. The reaction was performed at 343 K under 10-30 bar of H₂. The stirring speed was set at 700 rpm for all the reaction tests to eliminate the external mass transfer limitation. After the reaction was completed, the autoclave was cooled to room temperature and the H₂ was released. The catalyst powder was removed by 1400 rpm centrifugation and all the products in the solution were analyzed using a gas chromatograph (GC, Agilent, 7890B) equipped with a flame ionization detector (FID) and a CP-WAX 52 CB column (30 m $\times 0.25$ mm $\times 0.25$ µm), and tetradecane was the internal standard. The byproducts were identified by a gas chromatography-mass spectrometry (GC-MS, Agilent, 6890N-5973). The carbon balance was >99% in all the hydrogenation reactions. For recycling tests, the used catalyst after each reaction run was hot filtrated and separated, washed with ethanol several times, and then dried overnight for the next run.

2.5. H₂-D₂ exchange experiment

 H_2 - D_2 exchange experiments were performed in a fixed-bed reactor and the feeding gas consisted of 4 mL/min of H_2 , 4 mL/min of D_2 and 18 mL/ min of N_2 . A 15 mg portion of catalyst was loaded in the reactor. The exchange products of H_2 , HD and D_2 were analyzed with a QGA mass spectrometer (MS, Hiden Analytical Ltd.). Prior to the H_2 - D_2 exchange experiment, the sample was pretreated in N_2 at 120 °C for 30 min. After cooling to 70 °C, the gas was switched to the reactant gas composition to start the H_2 - D_2 exchange reaction with MS signal recording.

2.6. Adsorption experiment

The adsorption amounts of nitrobenzene reactant and aniline product on various Co/NC catalysts were measured by adding the sample (20 mg) into 5 mL of ethanol solution containing 20 µmol of the adsorbate. The suspension stirring was lasted for 40 min at room temperature and then the solid sample was filtered by centrifugation. The amount of the adsorbate remained in the supernate was measured with GC to determine the adsorption amount.

2.7. Electrochemical measurement

In consideration of the oxygen reduction reaction (ORR) reaction might provide the structural information of the active CoN_x sites in the Co/NC catalysts, the electrochemical activity measurement towards the ORR reaction was performed in a three-electrode cell using 0.1 M KOH electrolyte, a Pt sheet as counter electrode and a Ag/AgCl electrode as reference electrode. A rotating ring-disk electrode (Autolab, Metrohm) equipped with a glassy carbon disk (0.5 cm in diameter) was used as working

electrode. Co/NC catalyst (5 mg) was dispersed in 2.5 mL of solution (0.1 vol.% Nafion in ethanol and water) to obtain a final dispersion of the catalyst via sonication for 6 h. The dispersion (10 μ L) was pipetted on the newly polished disk electrode to prepare the working electrode. Linear sweep voltammetry (LSV) was measured in O₂ saturated 0.1 M KOH solution at 25 °C with a scanning rate of 20 mV/s and a rotation rate of 2000 rpm.

3. Results and discussion

3.1. Structural characterizations

The synthesis of Co/NC catalysts is achieved by simple pyrolysis treatment of starting materials of CoPc and melamine with different mixture ratios. According to the ICP-OES results, a series of as-prepared Co/NC catalysts have similar loading amount of Co species in the range of 27.8-30.2 wt.%, as listed in Table 1, indicating that structural evolution of the catalyst is centered on the formation of Co-based microstructure. It can be indirectly supported by the fact that the 'NC' sample has a remarkable low yield via same preparation process without mixing CoPc additive. Melamine determines the formation of Co/N-doped carbon sheet hybrids can indeed arise from thermolysis of mixed melamine and CoPc. The crystal phases are further characterized by the powder XRD patterns in Fig. 1A-E. The diffraction peak at 26.2° suggests that graphitic carbon forms during the pyrolysis. The diffraction peaks at 44.4°, 51.6° and 76.0° are assigned to metallic Co⁰ species [46]. Neither peaks of Co₃O₄ phase nor peaks of CoO phase are observed on the XRD patterns. The specific

surface areas of the catalysts are determined by the N₂ adsorption isotherms, as presented in Fig. 1F-J and Table 1. Relatively larger surface areas are obtained with 203 and 250 m²/g for Co/NC-0.30 and Co/NC-0.35 catalysts, respectively, whereas a low value of 53.6 m²/g is observed on Co/NC-0.15 catalyst. The TEM images in Fig. 2A-E display that the metallic Co⁰ particles are surrounded by typical bamboo-like nanofilaments, suggesting that the carbonization of melamine and the ligands in CoPc leads to the deposition of thin carbon layers at high treatment temperature. The statistical analyses of Co particle sizes in Fig. 2F-J demonstrate that the average size of Co particles varies with rising the amount of CoPc precursor addition. The average particle sizes of Co/NC-0.30, 0.35 and 0.45 catalysts are approximately 12-14 nm, which are dramatically smaller than that of Co/NC-0.15 catalyst (40 nm), as listed in Table 1.

The XPS spectroscopy is employed to reveal the electronic structure of N and Co species in the Co/NC catalysts. The N 1s core level spectra of the Co/NC catalysts in Fig. 3A-E can be deconvoluted into four types of N species, which are attributed to pyridinic (398.6 eV), pyrrolic (400.1 eV), graphitic (401.1 eV) and oxidative N species (402.8 eV) according to their binding energies [6,47]. The pyridine-type N species with the lowest binding energy are bound to a metal ion, while the pyrrole-type N species contribute two electrons to the carbon matrix [48,49]. Fig. 3F-J display the Co 2p 3/2 core level spectra that can be fitted by four components, i.e., metallic Co⁰ (778.6 eV), oxidative Coⁿ⁺ (779.8 eV), N-bonded Co species (781.2 eV) and satellite peak (785.6 eV) [50]. The quantitative results are summarized in Table 1 and the distributions of

these co-existed Co or N species are distinctly different for various Co/NC catalysts. Similar proportions of metallic Co^0 are observed with approximately 20% for all the catalysts. In particular, for two relative surface species of CoN_x and pyridinic N coordinated with Co atom, their distributions in the Co/NC catalysts exhibit volcanotype curves, as shown in Fig. 4. The maximal contents of both CoN_x and pyridinic N species are obtained on the Co/NC-0.30 catalyst. Either reducing or increasing the added amount of CoPc during catalyst synthesis causes lower contents of these two surface species. The existence of oxidative Co^{n+} species on the catalyst surface is further confirmed by the typical characteristic peaks of Co₃O₄ at 194, 469, 513, 617 and 675 cm⁻¹ on Raman spectra in Fig. 5 [51]. The Raman signals of defect-derived Dband at 1345 cm⁻¹ and graphite structure-derived G-band at 1585 cm⁻¹ also indicate that the catalyst surface consists of the defective graphitic carbon species [52]. All of these observations manifest that the composite structure of CoN_x-Co₃O₄ covered Co NPs and N-doped carbon layers have been prepared via the simple pyrolysis procedure.

3.2. Catalytic hydrogenation of nitrobenzene to aniline over Co/NC catalysts

The catalytic one-pot hydrogenation of nitrobenzene with H_2 is carried out on these Co/NC catalysts. In order to clearly understand their catalytic performances, several control reaction tests are firstly conducted. As shown in Table 2, the nitrobenzene hydrogenation into aniline cannot proceed in the absence of the catalyst (Entry 1) or H_2 atmosphere (Entry 2). In addition, no nitrobenzene conversion is observed over the starting material of CoPc (Entry 3 in Table 2) and the 'NC' catalyst (Entry 4 in Table 2) prepared by pyrolysis of melamine via the same procedure. Highly

selective hydrogenation of nitrobenzene to aniline without any detectable byproducts can be achieved on these Co/NC catalysts (Entries 5-11 in Table 2). These control experiment results demonstrate that neither pure CoPc complex with Co-N coordination sites nor non-Co-site 'NC' sample is capable of the hydrogenation of nitro group. The results also suggest that only the Co/N-doped carbon composite structure that is generated via high-temperature pyrolysis process can provide the catalytically active sites to accomplish the nitrobenzene-to-aniline transformation. Fig. 6 reveals a volcano-type curve for the relevance between catalytic hydrogenation activity (conversion of nitrobenzene) and adding amount of CoPc precursor during synthesis process of the Co/NC catalysts. The Co/NC-0.15 catalyst displays an unsatisfactory productivity of 6.7 mmol g_{Co}^{-1} h⁻¹ (Entry 5 in Table 2), however, under similarly high selectivity towards aniline as >99%, the Co/NC-0.30 and Co/NC-0.35 catalysts increase the activities by nearly eight times, reaching 53.8 and 51.8 mmol g_{Co}^{-1} h⁻¹ (Entries 8-9 in Table 2), respectively.

The catalytic activity of the Co/NC catalysts in nitrobenzene hydrogenation apparently depends on the pressure of feeding H₂ gas, e.g., a higher H₂ pressure promotes the reaction rate. The conversion of nitrobenzene increases from 41.0% to 94.3% and the corresponding productivity increases from 23.4 to 53.8 mmol g_{Co}^{-1} h⁻¹ (Entry 8 and Entries 12-13, Table 2) when the H₂ pressure raises from 10 to 30 bar. These results determine that all the hydrogenation reaction tests are performed with a fixed H₂ pressure at 30 bar. In considering that H₂ dissociation over the active metal-N_x sites should be one of the most critical affect factors for Co/NC-catalyzed

hydrogenation of nitrobenzene [53], the activity of the Co/NC catalysts towards H₂-D₂ exchange is measured. The H₂-D₂ exchange experiments are proceeded at 343 K that is the same with the temperature in nitrobenzene hydrogenation reaction, and the generation rates of gaseous HD product are recorded with an online MS. After cofeeding of 1:1 H₂ and D₂ (N₂ as balance gas), the steady state of HD generation with the maximum rate can be reached within different time durations, as shown in Fig. 7A. Fig. 7B summarizes the acceleration degrees (relative to the slope in Fig. 7A) and the attainable maximal H₂-D₂ exchange rates over the Co/NC catalysts. The obviously lower capability of H₂ dissociation for Co/NC-0.15 catalyst is possibly due to its larger average size of Co particles and a lower amount of CoN_x sites on the surface. Both Co/NC-0.30 and Co/NC-0.35 catalysts can rapidly reach the steady state within shorter time, compared to Co/NC-0.25 and Co/NC-0.45 catalysts. The rates of the H₂-D₂ exchange for the Co/NC catalysts are in sequence of Co/NC-0.30 > Co/NC-0.35 > Co/NC-0.45 > Co/NC-0.25 >> Co/NC-0.15, which is in line with the catalytic hydrogenation performances. The sequence in the H₂-D₂ exchange rates is apparently in accord with the order in the content of CoN_x surface species for all Co/NC catalysts. Furthermore, relatively larger surface areas (>200 m^2/g) and smaller particle sizes (approximately 12 nm) for Co/NC-0.30 and Co/NC-0.35 catalysts lead to more catalytically active CoN_x sites exposed on the catalyst surface, thus accelerating the H₂ dissociation process and entire hydrogenation reaction cycle.

In addition to the dissociative activation of H_2 molecule, the adsorption of nitrobenzene as the reactant and aniline as the product on these Co/NC catalyst surface

is also essential [54]. The adsorption amounts of nitrobenzene and aniline are measured on these Co/NC catalysts and the results are presented in Fig. 8. The small adsorption amounts of nitrobenzene are observed on Co/NC-0.15 and Co/NC-0.25 catalysts, which are 72.3 and 181 μ mol/g, respectively, as shown in Fig. 8A. Apparently large adsorption amounts of nitrobenzene (>300 μ mol/g) are obtained on Co/NC-0.30, 0.35 and 0.45 catalysts. A comparable level and a similar varying tendency for the adsorption amounts of aniline product are observed on these Co/NC catalysts (Fig. 8B). These results clearly suggest that enhanced adsorption for the reaction substrates contributes significantly to the catalytic hydrogenation reaction of nitrobenzene to aniline over the Co/NC catalysts. Combining of fast H₂ dissociation rate and high reactant adsorption ability strongly benefits the Co/NC-0.30 catalyst, affording satisfactory catalytic properties in the hydrogenation reaction.

It has been claimed that the coordinated CoN_x site rather than metallic Co or oxidative CoO_x is catalytically active towards the selective hydrogenation of nitro group in the functionalized arenes. Fortunately, the investigation on the CoN_x sites in the Co/NC catalysts might be accomplished by evaluating the activity in the electrochemically catalytic ORR reaction, since the isolated CoN_x site has also been reported as the active constituent for the ORR reaction [55-59]. The ORR reactions over the Co/NC catalysts are performed in O₂-saturated 0.1 M KOH electrolyte solution with a rotating disk electrode (2000 rpm of rotating rate). The linear sweep voltammetry (LSV) results in Fig. 9A indicate that Co/NC-0.30 catalyst shows the best ORR activity in term of the most positive half-wave potential ($E_{1/2}$) and the highest limiting diffusion

current density. The $E_{1/2}$ of Co/NC-0.30 catalyst is 0.815 V, which is 1.1, 1.4 and 18.5 mV more positive compared with that of Co/NC-0.35, Co/NC-0.25 and Co/NC-0.15 catalysts, respectively. Fig. 9B shows that the calculated current density of the optimal Co/NC-0.30 catalyst with 5.0 mA cm⁻² is at the top of a volcano-type curve that is perfectly corresponding to the distribution pattern of the CoN_x surface species for the Co/NC catalysts. These results demonstrate that more active CoN_x sites incorporated in the Co/NC catalysts can markedly facilitate not only the ORR reaction but also the nitrobenzene hydrogenation reaction. The catalytic performance comparison between two kinds of reactions can further explain the structure-activity relevance of Co/NC-type catalysts as expected. Therefore, surface CoN_x sites-enriched Co/NC-0.30 catalyst reveals a superior catalytic activity in both ORR reaction and nitrobenzene hydrogenation.

3.3. Reusability of Co/NC catalyst in nitrobenzene hydrogenation

The stability and reusability of the Co/NC catalyst in hydrogenation of nitrobenzene to aniline are also inspected under the studied reaction conditions. As presented in Fig. 10, the optimal Co/NC-0.30 catalyst displays >99% nitrobenzene conversion after 4 h, and such high activity can be maintained in the first three reaction runs. When half of the catalyst is used in the hydrogenation reaction, the nitrobenzene conversion is just reduced to approximately 50%, which can still be kept in further two reaction runs. The leaching of Co species into the solution generally causes the deactivation issue for Co catalysts, however, in the case of the Co/NC catalyst system, no Co species are detected in the spent reaction solution with ICP-OES examinations.

The structure of the spent Co/NC-0.30 catalyst after five-run reactions is characterized with XRD and Raman spectra. The XRD pattern in Fig. 11A reveals that no perceptible structural change is observed. The composite of graphitic carbon and metallic Co particles is still kept during the hydrogenation reactions. The Raman spectrum in Fig. 11B shows the vibration signals of Co₃O₄ and carbon phases that are coexisted in the spent Co/NC-0.30 catalyst, suggesting that the oxidative Co₃O₄ species on the surface of Co particles surrounded by the N-doped carbon layers are stable in reductive reaction conditions.

3.4. Catalytic hydrogenation of nitroarenes to substituted anilines over Co/NCcatalysts

Highly selective production of the industrially relevant anilines requires a generally applicable catalyst material. A wide variety of substituted nitroarenes, which are containing different kinds of groups such as halogen, aldehyde and nitrile, are employed to explore the catalytic hydrogenation selectivity of the optimal Co/NC-0.30 catalyst. The identical reaction conditions are used and the catalytic performances are summarized in Table 3. The halogen (iodo-, chloro- and fluoro-) moiety-substituted nitrobenzenes can be efficiently and selectively transformed into corresponding anilines (Entries 1-4 in Table 3). Although the dehalogenation process facilely occurs under the reaction conditions, the process can be completely suppressed in the presence of the Co/NC catalyst regardless of the number and the position of halogen moieties. The tolerance of bromo-group is also reflected by the high catalytic selectivity in the hydrogenation of the mixed-substituted nitroarene (Entry 5 in Table 3). For those

substances substituted with easily reducible moieties including methoxy-, nitrile- and formyl-moiety, the Co/NC-0.30 catalyst is still able to selectively activate and reduce the nitro-moiety with satisfactory activity (Entries 5-7 in Table 3). In addition, the activity and selectivity in catalytic hydrogenation cannot be effected by the presence of electron-deficient substituent (i.e. trifluoromethyl-group, Entries 8-9 in Table 3). However, the steric hindrance effect will cause the decline of the hydrogenation activity but not influence the high selectivity (Entry 10 in Table 3). Furthermore, Co/NC-0.30 catalyst can also efficiently achieve selective hydrogenation of the nitro-group located in the naphthalene ring (Entry 11 in Table 3). The above reaction results demonstrate that the Co in N-doped carbon matrix catalyst owns excellent catalytic activity and chemoselectivity for the direct hydrogenation of nitroarenes with H₂.

4. Conclusions

This work presents the Co in N-doped carbon matrix catalysts for selective hydrogenation of nitroarenes into corresponding anilines. The active Co/NC catalysts are prepared by a simple pyrolysis method with mixed CoPc complex and melamine as the Co, N and C precursors. The characterization results demonstrate that the catalysts are compositing of the oxidative Co_3O_4 and CoN_x -modified Co particles encapsulated by the N-doped carbon matrix. The optimal Co/NC catalyst posesses a relatively higher amount of active CoN_x sites, a smaller Co average particle size and a larger specific surface area, which can be regulated by the mixture ratio of two precursors. The isotope exchange, substance adsorption studies indicate that the excellent abilities of H₂ dissociation on the CoN_x active sites and reactant molecular adsorption can promote

the catalytic performance in nitro-group hydrogenation. Furthermore, the Co/NC catalyst can tolerate numerous moieties that are easily reducible or readily removable, and can also be used repeatedly without obvious activity loss.

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References

[1] R.S. Downing, P.J. Kunkeler, H. van Bekkum, Catal. Today 37 (1997) 121-136.

[2] R.A. Sheldon, H. van Bekkum, Fine Chemicals through Heterogeneous Catalysis,Wiley-VCH, Weinheim, 2001.

[3] P. Serna, A. Corma, ACS Catal. 5 (2015) 7114-7121.

- [4] R.A. Scheuerman, D. Tumelty, Tetrahedron Lett. 41 (2000) 6531-6535.
- [5] D.L. Yang, D. Fokas, J.Z. Li, L.B. Yu, C.M. Baldino, Synthesis (2005) 47-56.
- [6] X.L. Cui, Q.L. Zhang, M. Tian, Z.P. Dong, New J. Chem. 41 (2017) 10165-10173.
- [7] X.L. Cui, X. Zhou, Z.P. Dong, Catal. Commun. 107 (2018) 57-61.
- [8] S. Karami, B. Zeynizadeh, Z. Shokri, Cellulose 25 (2018) 3295-3305.
- [9] F. Yang, C. Chi, C.X. Wang, Y. Wang, Y.F. Li, Green Chem. 18 (2016) 4254-4262.
- [10] X. Ma, Y.X. Zhou, H. Liu, Y. Li, H.L. Jiang, Chem. Commun. 52 (2016) 7719-7722.

[11] J.-L. Sun, Y.-Z. Chen, B.-D. Ge, J.-H. Li, G.-M. Wang, ACS Appl. Mater. Interfaces (2018).

[12] J.G. de Vries, C.J. Elsevier, The Handbook of Homogeneous Hydrogenation,Wiley-VCH, Weinheim, 2007.

[13] P.G. Andersson, I.J. Munslow, Modern Reduction Methods, Wiley-VCH, Weinheim, 2008.

[14] Y.H. Dai, X. Gao, X.F. Chu, C.Y. Jiang, Y. Yao, Z. Guo, C.M. Zhou, C. Wang, H.M.Wang, Y.H. Yang, J. Catal. 364 (2018) 192-203.

[15] F.A. Harraz, S.E. El-Hout, H.M. Killa, I.A. Ibrahim, J. Catal. 286 (2012) 184-192.

[16] R.F. Nie, J.H. Wang, L.N. Wang, Y. Qin, P. Chen, Z.Y. Hou, Carbon 50 (2012) 586-596.

[17] C.H. Campos, M. Jofre, C.C. Torres, B. Pawelec, J.L.G. Fierro, P. Reyes, Appl. Catal. A-Gen. 482 (2014) 127-136.

[18] F. Cardenas-Lizana, S. Gomez-Quero, M.A. Keane, ChemSusChem 1 (2008) 215-221.

[19] F. Cardenas-Lizana, S. Gomez-Quero, M.A. Keane, Catal. Commun. 9 (2008) 475-481.

- [20] H.U. Blaser, H. Steiner, M. Studer, ChemCatChem 1 (2009) 210-221.
- [21] E.H. Boymans, P.T. Witte, D. Vogt, Catal. Sci. Technol. 5 (2015) 176-183.
- [22] A. Corma, P. Serna, Science 313 (2006) 332-334.
- [23] X. Sun, A.I. Olivos-Suarez, D. Osadchii, M.J.V. Romero, F. Kapteijn, J. Gascon,
- J. Catal. 357 (2018) 20-28.

[24] Z.Z. Wei, J. Wang, S.J. Mao, D.F. Su, H.Y. Jin, Y.H. Wang, F. Xu, H.R. Li, Y. Wang, ACS Catal. 5 (2015) 4783-4789.

- [25] R.M. Bullock, Science 342 (2013) 1054-1055.
- [26] K. Junge, B. Wendt, N. Shaikh, M. Beller, Chem. Commun. 46 (2010) 1769-1771.
- [27] R.V. Jagadeesh, D. Banerjee, P.B. Arockiam, H. Junge, K. Junge, M.M. Pohl, J.

Radnik, A. Bruckner, M. Beller, Green Chem. 17 (2015) 898-902.

- [28] G. Wienhofer, I. Sorribes, A. Boddien, F. Westerhaus, K. Junge, H. Junge, R.
- Llusar, M. Beller, J. Am. Chem. Soc. 133 (2011) 12875-12879.
- [29] F.A. Westerhaus, R.V. Jagadeesh, G. Wienhofer, M.M. Pohl, J. Radnik, A.E.
- Surkus, J. Rabeah, K. Junge, H. Junge, M. Nielsen, A. Bruckner, M. Beller, Nat. Chem. 5 (2013) 537-543.
- [30] R.V. Jagadeesh, A.E. Surkus, H. Junge, M.M. Pohl, J. Radnik, J. Rabeah, H.M.

Huan, V. Schunemann, A. Bruckner, M. Beller, Science 342 (2013) 1073-1076.

[31] L.C. Liu, P. Concepcion, A. Corma, J. Catal. 340 (2016) 1-9.

- [32] J. Wang, D.F. Gao, G.X. Wang, S. Miao, H.H. Wu, J.Y. Li, X.H. Bao, J. Mater. Chem. A 2 (2014) 20067-20074.
- [33] R.V. Jagadeesh, T. Stemmler, A.E. Surkus, M. Bauer, M.M. Pohl, J. Radnik, K.Junge, H. Junge, A. Bruckner, M. Beller, Nat. Protoc. 10 (2015) 916-926.
- [34] J.Y. Cao, X.D. Jia, M.W. Guo, Y.Y. Du, J. Xu, Z.D. Chen, Sustain. Energ. Fuels 2(2018) 169-174.
- [35] Y.Y. Sun, X.W. Li, Z.S. Cai, H.Z. Bai, G.P. Tang, Z.Y. Hou, Catal. Sci. Technol. 8 (2018) 4858-4863.
- [36] H.G. Huang, X.G. Wang, Y. Sheng, C.J. Chen, X.J. Zou, X.F. Shang, X.G. Lu, RSC Adv. 8 (2018) 8898-8909.
- [37] P. Ren, C. Sun, Y. Shi, P. Song, Y. Yang, Y. Li, J. Mater. Chem. C 7 (2019) 1934-1947.
- [38] X. Shi, Y. Yang, L. Wang, Y. Li, J. Phys. Chem. C 123 (2019) 4007-4021.
- [39] T. Stemmler, A.-E. Surkus, M.-M. Pohl, K. Junge, M. Beller, ChemSusChem 7 (2014) 3012-3016.
- [40] H. Jin, J. Wang, D. Su, Z. Wei, Z. Pang, Y. Wang, J. Am. Chem. Soc. 137 (2015)

2688-2694.

- [41] X. Sun, A.I. Olivos-Suarez, L. Oar-Arteta, E. Rozhko, D. Osadchii, A. Bavykina,
- F. Kapteijn, J. Gascon, ChemCatChem 9 (2017) 1854-1862.
- [42] T. Song, P. Ren, Y.A. Duan, Z.Z. Wang, X.F. Chen, Y. Yang, Green Chem. 20 (2018)10.
- [43] B. Tang, W.C. Song, E.C. Yang, X.J. Zhao, RSC Adv. 7 (2017) 1531-1539.
- [44] P. Zhou, C. Yu, L. Jiang, K. Lv, Z. Zhang, J. Catal. 352 (2017) 264-273.
- [45] X. Wang, W.X. Chen, L. Zhang, T. Yao, W. Liu, Y. Lin, H.X. Ju, J.C. Dong, L.R.
- Zheng, W.S. Yan, X.S. Zheng, Z.J. Li, X.Q. Wang, J. Yang, D.S. He, Y. Wang, Z.X.
- Deng, Y.E. Wu, Y.D. Li, J. Am. Chem. Soc. 139 (2017) 9419-9422.
- [46] J. Tang, R.R. Salunkhe, J. Liu, N.L. Torad, M. Imura, S. Furukawa, Y. Yamauchi,
- J. Am. Chem. Soc. 137 (2015) 1572-1580.
- [47] Z. Li, M. Shao, L. Zhou, R. Zhang, C. Zhang, M. Wei, D.G. Evans, X. Duan, Adv. Mater. 28 (2016) 2337-2344.
- [48] J.R. Pels, F. Kapteijn, J.A. Moulijn, Q. Zhu, K.M. Thomas, Carbon 33 (1995)1641-1653.
- [49] J. Casanovas, J.M. Ricart, J. Rubio, F. Illas, J.M. Jiménez-Mateos, J. Am. Chem. Soc. 118 (1996) 8071-8076.
- [50] J. Deng, H.J. Song, M.S. Cui, Y.P. Du, Y. Fu, ChemSusChem 7 (2014) 3334-3340.
- [51] S.L. Xiong, C.Z. Yuan, M.F. Zhang, B.J. Xi, Y.T. Qian, Chem.-Eur. J. 15 (2009) 5320-5326.
- [52] M.M. Lucchese, F. Stavale, E.H.M. Ferreira, C. Vilani, M.V.O. Moutinho, R.B.Capaz, C.A. Achete, A. Jorio, Carbon 48 (2010) 1592-1597.
- [53] L.C. Liu, F. Gao, P. Concepcion, A. Corma, J. Catal. 350 (2017) 218-225.
- [54] X.Y. Wan, C.M. Zhou, J.S. Chen, W.P. Deng, Q.H. Zhang, Y.H. Yang, Y. Wang,

ACS Catal. 4 (2014) 2175-2185.

[55] T. He, X.J. Wang, H.Q. Wu, H. Xue, P. Xue, J. Ma, M.L. Tan, S.H. He, R.J. Shen,

L.Z. Yi, Y. Zhang, J. Xiang, ACS Appl. Mater. Interfaces 9 (2017) 22490-22501.

[56] Y.Z. Chen, C.M. Wang, Z.Y. Wu, Y.J. Xiong, Q. Xu, S.H. Yu, H.L. Jiang, Adv.

Mater. 27 (2015) 5010-5016.

[57] X.L. Zhang, Z.X. Yang, Z.S. Lu, W.C. Wang, Carbon 130 (2018) 112-119.

[58] H.T. Yu, Y.C. Li, X.H. Li, L.Z. Fan, S.H. Yang, Chem. Eur. J. 20 (2014) 3457-3462.

[59] T. He, H. Xue, X.J. Wang, S.H. He, Y.L. Lei, Y.Y. Zhang, R.J. Shen, Y. Zhang, J.

Xiang, Nanoscale 9 (2017) 8341-8348.



Fig. 1. XRD patterns (A-E) and nitrogen adsorption-desorption isotherms (F-J) of

various Co/NC catalysts.



Fig. 2. TEM images and the particle size distributions of the Co/NC catalysts.



Fig. 3. XPS spectra of N 1s (A-E) and Co 2p 3/2 (F-J) of the Co/NC catalysts.



Fig. 4. Summarized distributions of surface CoN_x and pyridinic N species for various

Co/NC catalysts based on the XPS results.



Fig. 5. Raman spectra of the Co/NC catalysts.



Fig. 6. Catalytic performances of various Co/NC catalysts in hydrogenation of nitrobenzene to aniline. Reaction conditions: 30 mg of catalyst, 2 mmol of

nitrobenzene, 10 mL of ethanol, 30 bar of H_2 , 343 K, and 4 h.



Fig. 7. H_2 - D_2 exchange experiments on the Co/NC catalysts.





The adsorption was performed by addition of 20 mg catalyst into 5 mL of ethanol

solution containing 20 µmol substrate.



Fig. 9. (A) LSVs during ORR reactions for various Co/NC catalysts in O₂-saturated 0.1 M KOH with a sweep rate of 20 mV/s and a disk rotation rate of 2000 rpm. (B)

Summarized results of current density in the ORR reactions.



Fig. 10. Recycling tests of nitrobenzene hydrogenation over Co/NC-0.30 catalyst. Reaction conditions: 30 or 15 mg of catalyst, 2 mmol of nitrobenzene, 10 mL of

ethanol, 30 bar of H_2 , 343 K, and 4 h.



Fig. 11. XRD pattern (A) and Raman spectrum (B) of the spent Co/NC-0.30 catalyst.

Catalyst	Co wt.%	BET	NP	Surface Co species ^d			Surface N species ^d			
		area ^b	size ^c	(%)			(%)			
		(m ² /g)	(nm)	Co-N	Co-O	Co^0	Pyrid	Pyrro	Graph	Oxide
Co/NC-0.15	28.1	53.6	40.1	39.2	37.7	23.1	30.9	6.7	19.4	43.0
Co/NC-0.25	30.2	97.6	18.1	46.3	34.7	19.0	33.6	19.2	23.7	23.5
Co/NC-0.30	29.2	203	12.4	51.3	32.4	16.3	38.9	12.3	32.2	16.6
Co/NC-0.35	29.0	250	12.0	50.0	31.6	18.3	30.0	17.4	35.9	16.7
Co/NC-0.45	27.8	178	13.8	46.8	32.3	20.8	30.2	20.3	34.2	15.3

 Table 1. Structural information of various Co/NC catalysts.

^aCo loading amount was measured by ICP-OES results.

^bBET specific surface area was obtained from nitrogen adsorption isotherms.

^cNP (nanoparticle) size was analyzed from TEM images.

^dRelative ratios of surface Co and N species were obtained from XPS spectra of Co 2p 3/2 and N 1s orbits. Pyrid, Pyrro and Graph refer to pyridine, pyrrole and graphitic N species, respectively.

No.	Catalyst	Pressure	Conv.	Selec.	Productivity ^b
		(bar)	(%)	(%)	(mmol $g_{Co}^{-1} h^{-1}$)
1	No catalyst	30	/	/	/
2 ^c	Co/NC-0.30	30	/	/	1
3	CoPc	30	/	/	/
4 ^d	NC	30	/	/	
5	Co/NC-0.15	30	11.3	>99	6.7
6	Co/NC-0.20	30	13.4	>99	
7	Co/NC-0.25	30	36.7	>99	20.3
8	Co/NC-0.30	30	94.3	>99	53.8
9	Co/NC-0.35	30	90.1	>99	51.8
10	Co/NC-0.40	30	71.4	>99	/
11	Co/NC-0.45	30	63.9	>99	38.3
12	Co/NC-0.30	10	41.0	>99	23.4
13	Co/NC-0.30	20	69.6	>99	39.7

 Table 2. Catalytic performances of the prepared catalysts in nitrobenzene

 hydrogenation reactions.^a

^aReaction conditions: 30 mg of catalyst, 2 mmol of nitrobenzene, 10 mL of ethanol as solvent, 343 K, 30 bar of H₂, and 4 h.

^bCalculated by consumed nitrobenzene moles divided by total Co weight per hour.

^cHydrogenation reaction was performed in 30 bar of He gas.

^dNC catalyst was prepared by pyrolysis of unmixed melamine powder.

Entry	Substrate	Product	Conv. (%)	Selec. (%)
1		I NH ₂	99	>99
2	$F \longrightarrow NO_2$	$F \rightarrow NH_2$	97	>99
3		Cl	99	>99
4	$Cl \rightarrow NO_2$	Cl	99	>99
5	H ₃ CO-NO ₂ H ₂ CO	H ₃ CO H ₃ CO NH ₂	99	>97
6	OHC - NO ₂	OHC NH ₂	99	>98
7	NC-NO ₂	NC NH ₂	99	>99
8	O ₂ N OHC CF ₃	H ₂ N OHC — CF ₃	99	>98
9	NC CF ₃	NC CF ₃	99	>99
10	H ₃ C-CH ₃ CH ₃	H_3C H_3C H_3C H_3C H_3C H_3C H_3 H_2 H_3 H_3C H_3	75	>99
11	NO ₂	NH ₂	99	>99

Table 3. Co/NC-0.30-catalyzed hydrogenation of functionalized nitroarenes.^a

^aReaction conditions: 30 mg of Co/NC-0.30 catalyst, 2 mmol of nitrobenzene, 10 mL of ethanol as solvent, 70 $^{\circ}$ C, 30 bar of H₂, and 8 h.