

Very Important Paper

Self-Template Construction of High-Performance Co, N-Decorated Carbon Nanotubes from a Novel Cobalt Dicyandiamide Molecule

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N-doped carbon nanotubes (NCNTs) based composites have shown great prospect in catalysis relevant communities, which are often evolved from commercial CNTs and nitrogenous hybrid precursors. However, the direct fabrication of high-performance and non-noble metal uniformly embedded NCNTs from a single molecule level without foreign ions remains a thorny issue. Herein, we firstly report a high surface area and large diameter NCNTs (215.7 m²g⁻¹, 150 nm) embedded with Co NPs and atomically dispersed CoN_x active sites via a facile and self-template pyrolysis of a novel synthesized cobalt

1. Introduction

Carbon nanotubes (CNTs) are broadly explored to be excellent support for loading multiple active sites owing to their superior stability, conductivity, and recyclability. Thus, considerable efforts have been devoted to the design and development of efficient CNTs-based composites via grafting, confinement and deposition-precipitation methods because of the high accessible surface area, uniform pore size and ingenious modifiability of CNTs.^[1] It has been shown that the CNTs anchored non-noble metal catalysts can display analogous catalytic properties to those of precious metals in some specific reactions, such as the electrochemical H₂O splitting, oxygen reduction reaction (ORR), Li–S batteries and CO₂RR.^[2] However, it is often difficult to embed non-noble metal active sites evenly into the inner and outer surface of CNTs by traditional methods due to the

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	Supporting information for this article is available on the WWW under https://doi.org/10.1002/cctc.202100228

dicyanamide molecule. The resulting Co@NCNTs-800 catalyst exhibits superior catalytic activity toward nitrobenzene hydrogenation compared to the catalyst prepared from a mixture of dicyandiamide and CoCl₂ under mild conditions (>99% vs. 1.3% conversion). Furthermore, it also presents a prominent activity and selectivity for the hydrogenation of various nitroaromatics, and possesses the best catalytic performance compared to the existing non-noble metal-based heterogeneous catalytic systems.

hydrophobic property, narrow pore size and lack of strong anchoring sites of the inherent ${\rm CNTs.}^{\scriptscriptstyle [3]}$

Revealingly, the Lee's group prepared a stable Fe-porphyrinlike CNTs catalyst via plasma-enhanced CVD strategy, which showed prominent ORR catalytic performance due to the presence of a great number of pyridinic-N species, high degree of defect and edge exposure as well as the solidly inlaid Fe-N₄ active site.^[4] Such diversified non-noble metal and nitrogen codecorated carbon nanotubes (M@NCNTs) catalysts are also discovered to be a promising candidate toward hydrogenation reactions.^[5] And then several approaches have been developed to fabricate M@NCNTs and related non-noble metal based Ndoped carbon catalysts,^[6] which can greatly improve the hydrogenation performance of non-noble metal even without the addition of trace second noble metal component.^[7] Nevertheless, these synthetic strategies generally require various hard templates, complicated procedure and highly toxic corrosive, which greatly restrict their further application.^[8] Alternatively, employing metal salts and C, N-containing organic matter as hybrid precursors followed by multistep pyrolysis can fabricate the M@NCNTs catalysts, which prevent the use of toxic etching agents.^[9] But these approaches inevitably incorporate different foreign ions, such as alkali metal ions and halogen anions before pyrolysis, which can bring about unfavorable impacts on the morphology, metal dispersion and catalytic activity of M@NCNTs catalysts.^[10] Thus, it is urgent to develop a high performance and large diameter M@NCNTs catalysts with highly exposed active sites directly from a facile and self-template pyrolysis of a single-molecular level without introducing any foreign ions.

Herein, we present, for the first time, a simple and efficient approach towards the fabrication of bamboo-like Co@NCNTs-T (T=700~1000°C) catalysts via controlled self-template pyroly-



sis of a novel synthesized cobalt dicyanamide [Co(dca)₂] precursor under flowing N₂. Unexpectedly, the resulting Co, Ndecorated CNTs simultaneously possesses a large surface area (215.7 m²g⁻¹), spacious interior cavity (>100 nm), uniform distribution of metal species as well as the high N content (2.60 wt%). The resultant Co@NCNTs-800 catalyst as a representative not only presents an superior catalytic performance in the hydrogenation of nitrobenzene under extremely mild conditions (both of the conversion and selectivity > 99%, 40°C, 0.1 MPa H₂, 3 h), but also exhibits prominent activity and selectivity for the hydrogenation of various nitroaromatics and displays an optimal catalytic performance compared to the existing non-noble metal-based catalytic systems. Thus, it brings up a promising avenue for design and preparation of excellent non-noble metal-based NCNTs catalysts for potential fine chemicals transformation.

Experimental section

Materials and methods

Dicyandiamide and $NaN(CN)_2$ (96%) were purchased from Meryer Co., Ltd. $CoCl_2$, AgNO₃ and concentrated HCl were purchased from Sinopharm Chemical Reagent Co., Ltd. FeBr₂, CoBr₂ and NiBr₂ were purchased from Alfa Aesar Co., Ltd. Nitrobenzene and its derivatives were provided by Aladdin Chemical Reagent Co., Ltd. All of other chemicals were used as received without any further purification. Deionized water was used throughout the entire experiment.

Synthesis of metal dicyanamide precursor $(M(dca)_2, M = Fe, Co, Ni)$

8.6 g of AgNO₃ was dissolved in 100 mL of deionized water, and then 4.5 g of NaN(CN)₂ was slowly added into the above solution under stirring. After 2 h of reaction, the generated suspension was filtered and washed with an excess amount of deionized water, obtaining the white AgN(CN)₂ solid. Then, it was transferred into a 250 mL three-neck flask, and 100 mL of CoBr₂ solution in a constant pressure funnel was dropped into the flask with assistance of violent agitation. The mixture was continuously stirred for 2 h followed by filtration to remove the light yellow precipitate. The pink filtrate was treated via vacuum-rotary evaporation and the resultant Co(dca)₂ pink solid was dried overnight under 80 °C (Elemental analysis for C_4N_6Co , calculated: C, 25.13%, N, 43.98%; Found: C, 24.57%, N, 43.84%; ICP-OES: 32.05 wt% Co content). As a comparison, the identical procedure was applied to prepare Fe(dca)₂ and Ni(dca)₂ except for using FeBr₂ and NiBr₂ as starting material.

Synthesis of NCNTs embedded cobalt catalyst (Co@NCNTs-T)

Co(dca)₂ was placed into ceramic boat and pyrolyzed at 700~ 1000 °C for 2 h under flowing N₂ gas in the tube furnace and then cooled naturally to room temperature. After that, the obtained black product was etched with 1.0 M HCl solution for 24 h to remove unstable and inactive Co species and then thoroughly washed with deionized water. Finally, N-doped carbon nanotubes embedded cobalt catalyst was obtained by heat-treatment again at 700 °C for 1 h under flowing N₂ (denoted as Co@NCNTs–T, T refers to the pyrolysis temperature). The content of Co in Co@NCNTs-800 catalyst was analyzed by SEM-EDS to be 4.12 wt%. As comparison,

General procedure for the selective hydrogenation of nitroaromatics

1.0 mmol of nitroaromatics, 40 mg of Co@NCNTs–T catalyst and 5.0 mL of ethanol were added into a 35 mL glass reaction vial. After flushing 3 times with H_2 , the pressure was maintained at 0.1 MPa at room temperature. The mixture was heated to the set temperature with magnetic stirring for a certain time. After completion of the reaction, the catalyst was removed from the mixture by centrifugation, and the liquid phase was analyzed by GC or GC-MS with n-tetradecane as internal standard.

Material characterization

Transmission electron microscope (TEM) was carried out on a FEI Tecnai G2 F20S-Twin using an accelerating voltage of 200 kV. For sample preparation, the powders were dispersed in ethanol with the assistance of ultrasonication, and then one drop of the solution was dropped onto a micro grid. XRD measurements were performed on a Rigaku Ultima IV diffractometer using Cu-K α radiation as the X-ray source in the 2θ range of $10-90^{\circ}$. The N₂ adsorption-desorption isotherms were obtained on an ASAP2020 analyzer. Before measurement, samples were degassed under vacuum at 120 $^\circ C$ for 6 h. Surface area of the samples was calculated by the Brunauer-Emmet-Teller (BET) method, and their pore volume and pore size distribution were calculated using the Barrett-Joyner-Halenda (BJH) model. Thermogravimetric analysis (TGA) was determined on a Setaram Labsys Evo apparatus. The samples were heated in an alumina pan from 30 to 1000°C at a heating rate of $10\,^\circ C \cdot \text{min}^{-1}$ under flowing N_{2^*} Fourier transform infrared (FT-IR) spectra were obtained using a Nicolet iS5 spectrophotometer with KBr pellet. The cobalt loading amount of Co@NCNTs-800 catalyst was determined by NexION 350 inductively coupled plasma mass spectrometry (ICP-OES). The X-ray photoelectron spectra (XPS) was analyzed on the PHI-5702 instrument and the C1s line at 284.5 eV was used as the binding energy reference.

2. Results and discussion

The indisputable fact is that the non-noble transition metals Fe, Co, Ni etc. can be transformed into efficient heterogeneous catalyst during in-situ pyrolysis and growth of carbon-based composites from different types of nitrogenous hybrid precursors. At present, we choose the Co(dca)₂ molecule as an original material is that the organic cyano groups serve as both C, N sources and coupling units to effectively construct the cobaltembedded polymer networks, while the Co species facilitate the formation of NCNTs during pyrolysis process without introducing any foreign ions. Schematic illustration of the general procedure for the fabrication of Co@NCNTs-T catalyst is displayed in Scheme 1. Briefly, the Co(dca)₂ monomer is synthesized utilizing a facile precipitation-displacement method, which is acted as C, N, Co sources and pore-forming agent simultaneously (Figure S1 and Figure S2). The coordinated Co ions are firstly embedded into the polymer frameworks by





Scheme 1. Schematic illustration of the synthesis of Co@NCNTs-800 catalyst (Note: purple ball represents Co and blue ball represents N element).

cross-linking condensation of cyano groups at relatively low temperature. Subsequently, the generated Co species under carbothermal conditions can efficiently catalyze the reorganization and graphitization of polymer networks, leading to the generation of Co@NCNTs–T catalyst.

The morphology evolution process of Co@NCNTs–T samples are shown in Figure 1a–d. It can be clearly observed that a plentiful of rough, irregular, and open NCNTs are generated when Co(dca)₂ monomer is pyrolyzed at 700 °C (Figure 1a, Figure S3 and S4). Then, these nanotubes become more compact and uniform upon elevating the temperature to 800 °C (Figure 1b). As pyrolysis temperature continues to increase, it will cause the nanotubes to aggregate slightly at 900 °C and eventually collapse seriously at 1000 °C due to the continuous increase of Co NPs and their thermal etching effect (Figure 1c and 1d).^[9a] TEM images further reveal the distinct bamboo-like structure of the Co@NCNTs-800 catalyst. As shown in Figure 1h, the mean diameter of the nanotubes is determined to be approximately 150 nm and the surface of the tubular structure is rough with obvious wrinkles. Interestingly, all of the NCNTs are completely hollow and individual Co NPs are encapsulated by a thin layer of N-doped carbon (Figure 1f and Figure S5). HAADF-STEM and corresponding elemental mapping images of the Co@NCNTs-800 catalyst obviously reveal the uniform



Figure 1. (a–d) SEM images of Co@NCNTs–T (T=700–1000 °C), (e, h) TEM, (f, i) HRTEM, (g, j) HAADF-STEM images and the corresponding EDS elemental mapping images of Co@NCNTs-800 catalyst.



distribution of C, N, O and Co elements within hollow nanotubes framework (Figure S6). Surprisingly, a large number of uniformly distributed and monodispersed Co signals are also detected on NCNTs surface except for individual strong Co NPs signals (Figure 1g, 1j and Figure S11). It can be speculated that the encapsulated Co NPs combined with atomically dispersed CoN_x sites coexist in NCNTs.

XRD diffraction peak of Co@NCNTs-T at 26.2° is assigned to the (002) reflection of graphic-type lattice and diffraction peaks at 44.2, 51.5 and 75.8° can be assigned to the (111), (200) and (220) planes of face-centered cubic Co NPs (Figure 2a).^[11] Raman spectra of Co@NCNTs-T display the characteristic D band at \sim 1350 cm⁻¹ and G band at \sim 1610 cm⁻¹ assigned to disordered sp³ carbon and graphitic sp² carbon, respectively (Figure 2b). The high I_D/I_G value indicates the formation of defective carbon nanotubes, which mainly originate from the successful doping of Co and N elements into the NCNTs framework during the pyrolysis of Co(dca)₂ molecule.^[12] The peaks at 3432 cm⁻¹ and 1626 cm⁻¹ in FT-IR spectra correlate well with the stretching and bending vibration of -N-H bond, while the peak at 1087 cm^{-1} is attributed to the stretching vibration of -C-Nbond in Co@NCNTs-T (Figure S8). N₂ sorption-desorption measurement was further conducted to investigate the surface area and pore size distribution of the Co@NCNTs–T catalysts (Table S1). As shown in Figure 2c, all of the samples display distinct type IV curve, which demonstrate the typical mesoporous structure (Figure S7). The BET surface area, pore volume and average pore diameter of the representative Co@NCNTs-800 catalyst are calculated to be 215.7 m²g⁻¹, 1.371 cm³g⁻¹ and 3.94 nm. Elemental analysis displays that the N content in Co@NCNTs-800 is about 2.60 wt%, suggesting that the N species are well incorporated into the NCNTs skeleton. Thus, it is feasible to fabricate the high surface area and large diameter Co@NCNTs–T catalysts from the self-developed Co(dca)₂ molecule.

The surface constituents and chemical state of the Co@NCNTs—T were analyzed by X-ray photoelectron spectroscopy (XPS). As shown in Figure 3, the high-resolution N1s spectra of Co@NCNTs—T catalysts can be deconvoluted into four different types of nitrogen species, namely pyridinic-N (~ 398 ± 0.5 eV), pyrrolic-N (~ 399.8 ± 0.9 eV), graphitic-N (~ 401 ± 0.3 eV) and pyridine N-oxide (~ 404.8 ± 0.9 eV).^[13] Among them, the graphitic-N accounts for a large proportion, proving the excellent graphitization of these catalysts (Figure S10 and Table S2). In high-resolution Co2p spectra (Figure 2d and Figure S9), the characteristic peak at ~778.5 eV assigned to



Figure 2. (a) XRD patterns, (b) Raman spectra, (c) N_2 adsorption-desorption isotherms of Co@NCNTs-T (T=700-1000 °C) and (d) Co 2p spectrum of Co@NCNTs-800 catalyst.

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Figure 3. High-resolution XPS in N1s spectra of (a) Co@NCNTs-700, (b) Co@NCNTs-800, (c) Co@NCNTs-900 and (d) Co@NCNTs-1000 catalysts.

metallic Co NPs is absent, demonstrating that bare Co NPs on the surface of Co@NCNTs—T are completely removed. Instead, two peaks at ~779 eV and ~782 eV correspond to N-doped carbon encapsulated Co NPs and atomically dispersed CoN_x.^[14] These two Co2p_{3/2} peaks show ~0.5 eV shift to a higher bonding energy compared with the references.^[2e] The positive shift suggests the existence of strong electron interaction between Co species and NCNTs support.

To further confirm the co-existence of N-doped carbon encapsulated Co NPs and atomically dispersed CoN_x sites in Co@NCNTs-800 catalyst, X-ray absorption fine structure (XANES) and extended X-ray absorption fine structure (EXAFS) were carried out to demonstrate the electronic states (Figure 4). It can be seen that the absorption edge position of Co@NCNTs-800 is located between the Co foil and CoPc, indicating the valence of Co is situated between 0 and +2. The Fourier-transformed (FT) k³-weighted EXAFS of Co@NCNTs-800 displays two coordination peaks at 1.49 Å and 2.12 Å as compared to reference samples, which are ascribed to Co–N and Co–Co mode, respectively. The results further corroborate the evidence

that the N-doped carbon encapsulated Co NPs and atomically dispersed CoN_x in Co@NCNTs-800 catalyst.

The benchmark reaction of selective hydrogenation of nitrobenzene was carried out to evaluate the catalytic performance of as-synthesized non-noble metal based catalysts (Figure S13). Among the Co-based catalysts with different pyrolysis temperature, Co@NCNTs-800 shows the optimal catalytic activity, which can completely convert the nitrobenzene into aniline under mild conditions (Table 1, entry 3 and Table S5). In contrast, Fe@NCNTs-800 and Ni@NCNTs-800 are almost no activity for hydrogenation of nitrobenzene. The Co-DCDA-800 and Co-NaDCA-800 catalysts (TEM results are shown in Figure S12) also exhibit slight activity under identical conditions, which demonstrate that the involvement of other foreign ions (Cl⁻ or Na⁺) during the preparation of Co-based N-doped carbon by pyrolysis strategy is fatal to the selective hydrogenation of nitrobenzene. The extraordinary activity of Co@NCNTs-800 can be attributed to the high exposed surface area, strong bonding, and electronic effect between Co species and NCNTs, which is helpful for the formation of highly accessible catalytically active CoN_x site during in-situ carbon-





Figure 4. XANES spectra at the Co K-edge of (a) Co foil, CoPc and Co@NCNTs-800 and (b) Fourier transformed (FT) k^3 -weighted χ (k)-function of the EXAFS spectra for Co K-edge.

Table 1. Selective hydrogenation of nitrobenzene by different Co-based catalysts. ^[a]									
Entry	Catalyst	t [h]	Conv. [%] ^[b]	Sel. [%] ^[b]					
1	Co@g–C ₃ N ₄ -550	3	0	0					
2	Co@NCNTs-700	3	57.6	> 99					
3	Co@NCNTs-800	3	>99	> 99					
4	Co@NCNTs-900	3	57.7	> 99					
5	Co@NCNTs-1000	3	35.0	> 99					
6	Fe@NCNTs-800	3	<1	-					
7	Ni@NCNTs-800	3	<1	-					
8 ^[c]	Co–DCDA-800	3	1.3	>99					
9 ^[d]	Co-NaDCA-800	3	1.4	>99					
10 ^[e]	Co@NCNTs-800	3	35.2	>99					
11 ^[f]	Co@NCNTs-800	5	92	>99					
(10) ···									

[a] Reaction conditions: 1.0 mmol of nitrobenzene, 40 mg of catalyst, 5.0 mL of EtOH, 40 °C, 0.1 MPa of H₂, [b] Conversion and Selectivity were analyzed by GC-FID and n-tetradecane was used as internal standard, [c] DCDA: dicyandiamide, [d] NaDCA: sodium dicyanamide, [e] 10 mg KSCN was added, [f] after run 3 times.

ization and reduction process. As is well-known, KSCN is often used as a poisoning agent for coordination and poisoning of atomically dispersed active sites of metals.^[15] To distinguish the contribution of N-doped carbon encapsulated Co NPs and CoN_x in hydrogenation, different amounts of KSCN poisoning agent were added to the catalytic system to study the catalytic performance of the Co@NCNTs-800 catalyst. On account of Co NPs are firmly wrapped by N-doped carbon layers (Co NPs dispersed on NCNTs surface have been removed by HCl), and hence the highly exposed CoN_x sites in NCNTs are likely to be preferentially poisoned by KSCN. Consequently, the atomically dispersed CoN_x sites are more inclined to be coordinated and poisoned by KSCN molecule. Obviously, the conversion of nitrobenzene decreased dramatically from >99% to 5.4% as the amount of KSCN increased from 10 to 100 mg, demonstrating the dominant function of CoN_x active site. The results indicate that the active site should be highly exposed CoN_x rather than the N-doped carbon coated Co NPs. Thus, the contribution of N-doped carbon coated Co NPs in Co@NCNTs-800 is negligible (Table S4). As shown in Table S3, the CNTs and NCNT support have no catalytic activity for hydrogenation of nitrobenzene. For Co-doped CNT sample, its catalytic activity

also can be neglected, implying that the Co NPs are not the active centers in the catalytic system. Moreover, the Co@NCNTs-800 catalyst still retains high activity and selectivity for hydrogenation of nitrobenzene after running 3 times (Table 1, entry 11).

To further confirm the universality of on-hand Co@NCNTs-800 catalyst, different substituted nitrobenzene derivatives were also investigated. As summarized in Table 2, 4-fluoronitrobenzene is transformed into the corresponding 4-fluoroaniline with >99% conversion and selectivity (Table 2, entry 2). 2-Cl and 4-Cl substituted nitrobenzene can be quantitatively transformed into target amine products when the reaction time is slightly prolonged. The hydrogenation of other nitroaromatic substrates also possesses more than 95% conversion and >99% selectivity, whatever the substituent is electron-donating or electron-withdrawing on the benzene ring (Table 2, entries 5-9). Overall, the hydrogenation of nitroaromatics is slightly affected by substituents on the nitrobenzene, in which the substrates with electron-donating groups proceed more smoothly than the electron-withdrawing groups. More significantly, the phenomenon of de-halogenation and over-hydrogenation can be completely suppressed in the presence of





analyzed by GC-FID and n-tetradecane was used as internal standard, [c] 0.5 mmol of substrate.

Co@NCNTs-800 catalyst, which further corroborate the superior catalytic selectivity for various nitroaromatics (Table 2, entries 3, 8 and 9).^[13] Additionally, the comparison of catalytic performance of nitrobenzene hydrogenation with recently reported representative non-noble metal based catalysts are shown in Table 3. It can be seen that the current Co@NCNTs-800 catalyst still exhibits superior catalytic activity and selectivity even under extremely mild conditions (40 °C, 0.1 MPa H₂, 3.0 h).^[14]

3. Conclusions

In summary, we have developed a facile and novel strategy for fabricating Co, N-decorated carbon nanotube with ultra-large inner diameter through one-step pyrolysis of a simple $Co(dca)_2$ monomer. Both of the CoN_x and encapsulated Co NPs are well-dispersed in the high surface area and large diameter N-doped carbon nanotubes, and the actual active site for hydrogenation of nitrobenzene derivatives should be highly exposed CoN_x . The prepared Co@NCNTs-800 catalyst exhibits superior catalytic



Table 3. Comparison of the catalytic performance of nitrobenzene hydrogenation with recently reported representative non-noble metal based catalysts.									
Catalyst	T [°C]	P [MPa]	t [h]	Conv. [%]	Sel.[%]	References			
Co@NCNTs-800	40	0.1	3.0	>99	>99	This work			
Co-N _x /C-800-AT	110	0.35	1.5	100	> 99	[14a]			
Co@mesoNC	110	3.0	3.0	> 99	> 99	[14b]			
LaCu _{0.67} Si _{1.33}	120	6.0	60	> 99	99	[14c]			
Co–Mo–S-0.39-180	150	1.1	7.0	>99	>99	[14d]			
Co@SiCN	110	5.0	15	> 99	> 99	[14e]			
Co–Co ₃ O ₄ @Carbon-700	110	4.0	6	>99	>99	[14f]			
Fe-phen/C-800	120	5.0	12	>99	>99	[14 g]			
Co–L ₁ /Carbon	110	5.0	4.0	>99	95	[14 h]			
CoO _x @NCNTs	110	3.0	7.0	>99	98	[14i]			
Ni-in-ANTs	110	2.0	4	>99	>99	[15]			

activity toward hydrogenation of nitrobenzene under extremely mild condition, which is 76-fold as high as the Co-DCDA-800 catalyst prepared by simple physical mixture. Furthermore, it also performs a remarkable catalytic activity and selectivity for various nitroaromatic derivatives. The findings open up a new avenue to design and prepare efficient and robust non-noble metal based M@NCNTs catalysts for fine chemicals transformation and clean energy production.

Supporting Information

The synthesis procedure of metal dicyanamide precursor [M-(dca)₂]; FT-IR spectra of as synthesized cobalt dicyanamide and NaN(CN)₂ raw material; TGA curve of the as-synthesized cobalt dicyanamide complex; SEM images of the as-prepared Co@NCNTs–T (T=700–1000 $^\circ\text{C}$) catalysts; HAADF-STEM image and the corresponding line and surface scanning mode of Co@NCNTs-800 catalyst; The pore size distribution and N-type distribution of Co@NCNTs-T (T=700-1000 °C) catalysts; FT-IR spectra, High-resolution XPS in N1s spectra and High-resolution XPS in Co2p spectra of the as-prepared Co@NCNTs-T (T=700-1000 °C) catalysts; The results of N₂ adsorption-desorption and elemental analysis for different Co-based catalysts; The selective hydrogenation of nitrobenzene with different catalysts; The selective hydrogenation of nitrobenzene by Co@NCNTs-800 with different KSCN added; Selective hydrogenation of nitrobenzene under various reaction conditions; The possible reaction mechanism of nitrobenzene hydrogenation.

Acknowledgments

This work is supported by National Natural Science Foundation of China (21703129, 221173137). And we are also very grateful for the test platform provided by Shanxi University of Scientific Instrument Center.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Cobalt dicyanamide \cdot self-template strategy \cdot N-doped carbon nanotubes \cdot CoN_x active site \cdot nitroaromatics hydrogenation

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Manuscript received: February 10, 2021 Revised manuscript received: March 9, 2021 Accepted manuscript online: March 17, 2021 Version of record online:

FULL PAPERS



Self templating: A high surface area and large diameter NCNTs (215.7 m^2g^{-1} , 150 nm) embedded with atomically dispersed CoN_x active site is fabricated via a facile and selftemplate pyrolysis of a novel synthesized cobalt dicyanamide molecule, which exhibits superior catalytic activity toward nitrobenzene hydrogenation compared to the catalyst prepared from a mixture of dicyandiamide and CoCl₂ under mild conditions (> 99% vs. 1.3% conversion). J. Li, S. Chen, M. Liu, Z. Li, Z. Dong*, Dr. F. Zhang*, X.-M. Zhang*

1 – 10

Self-Template Construction of High-Performance Co, N-Decorated Carbon Nanotubes from a Novel Cobalt Dicyandiamide Molecule