



Heterogeneous & Homogeneous & Bio- & Nano-

CHEM **CAT** CHEM

CATALYSIS

Accepted Article

Title: Co Nanoparticles Encapsulated in Nitrogen Doped Carbon Tubes for Efficient Hydrogenation of Quinoline under Mild Conditions

Authors: Ruirui Yun, Lirui Hong, Wanjiao Ma, Ruiyu Zhang, Feiyang Zhan, Baishu Zheng, Jingui Duan, and Suna Wang

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *ChemCatChem* 10.1002/cctc.201901641

Link to VoR: <http://dx.doi.org/10.1002/cctc.201901641>

WILEY-VCH

www.chemcatchem.org



Co Nanoparticles Encapsulated in Nitrogen Doped Carbon Tubes for Efficient Hydrogenation of Quinoline under Mild Conditions

Ruirui Yun,* Lirui Hong, Wanjiao Ma, Ruiyu Zhang, Feiyang Zhan, Jingui Duan,* Baishu Zheng, and Suna Wang*

Prof. R. Yun, Dr. L. Hong, W. Ma, Dr. R. Zhang and F. Zhan

The Key Laboratory of Functional Molecular Solids, Ministry of Education, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, P. R. China.

E-mail: ruirui58@ahnu.edu.cn

Prof. S. Wang

Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, P. R. China

E-mail: wangsun@luc.edu.cn

Prof. B. Zheng

School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201, P. R. China

Prof. J. Duan

College of Chemical Engineering, Nanjing Tech University, Nanjing 210001, P. R. China

E-mail: duanjingui@njtech.edu.cn

ABSTRACT: The hydrogenation of nitrogen-containing heterocyclic precursors in aqueous medium is quite challenging, especially at low temperature and without imposing molecular hydrogen pressure. In the light of the edges of metal nanoparticles (NPs) possess high selective activity, but most of the exposed metal surface does not. Hence, to influence the activity of the entire NPs surface, the use of zeolitic imidazolate frameworks (ZIFs) to obtain the metal NPs encapsulated in the carbon tubes which has been applied frequently. Herein, we design and synthesize a series of metal catalysts encapsulated in N-doped carbon nanotubes (NCT), which disperse on the hollow N-doped carbon framework (HNC), via pyrolysis ZIF-67, ZIF-67@ZIF-8, and ZIF-8@ZIF-67 step by step. The catalyst of Co@NCT/HNC shows outstanding activity of hydrogenation of quinoline under mild conditions, due to the

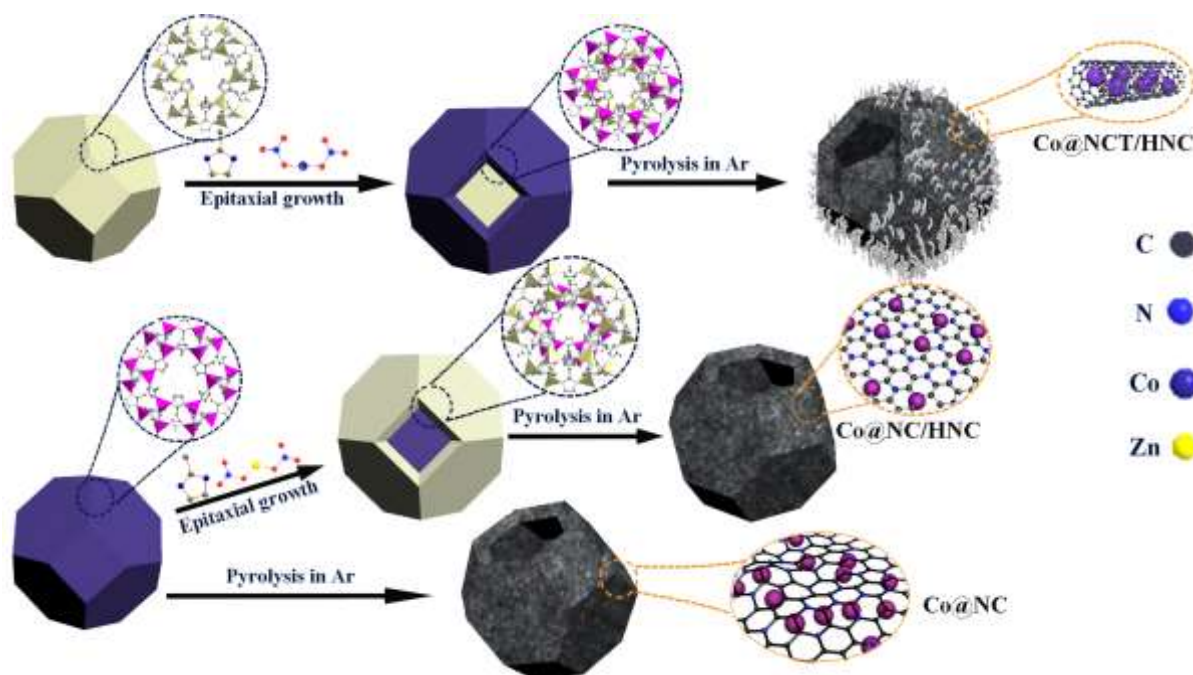
synergistic effects between Co NPs, NCT and HNC, such as the NCT make the hydrogen reach the surface of the reactant rapidly, and the encapsulated structure can enormously prevent the metal aggregating.

In the field of organic synthesis and industrial chemistry, the selective hydrogenation of functional groups (such as C=C, C=O and C=N et al) plays crucial roles.^[1] For instance, as important building blocks of many organic intermediates, agrochemicals and pharmaceutical intermediates, 1, 2, 3, 4-tetrahydroquinoline (py-THQ) has attracted a great deal of attention.^[2] In recent years, heterogeneous catalysts show a wide range of applications in quinoline hydrogenation, especially for precious metal catalysts, that possess extraordinary effects under mild conditions, such as Pt,^[3] Pd,^[4] Ru,^[5] Rh,^[6] Ir,^[7] and Au^[8] and so on. However, there are still lots of shortcomings, including lower reserves, higher costs, the need for corresponding ancillary groups, and poor chemo-selectivity when more than one functional groups are involved. Moreover, noble metal catalysts typically need high pressure H₂ as a source of hydrogen,^[9] which leads to high risk, no matter what in laboratory storage and usage.

Currently, the hydrogen sources much more used by researchers are formic acid (FA) and ammonia borane (AB).^[10] FA is a good substitute for hydrogen because it has a high hydrogen content and easy to precipitate. Nevertheless, it often produces carbon dioxide or monoxide in the dehydration process, where carbon monoxide may poison the catalysts and reduce the life of catalysts significantly. AB possesses very high hydrogen content, up to 19.6 wt%.^[11] It can be seen from the dehydration pathway ($\text{NH}_3\text{BH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{BO}_2 + 3\text{H}_2$) that one equivalent of AB can produce three equivalents of hydrogen, while the reaction conditions are mild. Studies have shown that many metal catalysts can accelerate the hydrogen evolution from AB, but they are not able to catalyze the hydrogenation of some functional groups from organics. Consequently, it is necessary to improve the catalytic ability and selectivity of the catalysts by rational design of the synthetic route.

In recent years, non-precious metal catalysts are attracting increasing attention due to their excellent performance in hydrogenation reactions. Moreover, non-noble metal has marvelous content, and a rational design may endow better catalytic selectivity. In particular, transition metal loaded on porous carbon such as Fe,^[12] Co,^[13] and Ni^[14] are widely used. However, the metal nanoparticles are often constructed from high temperature pyrolysis which may induce the phenomenon of metal aggregation, and that the aggregation will lead to the reduction of metal dispersion and active sites, further hindering the performance of the catalyst. Meanwhile, the metal will be leached during the reaction.^[15]

Given the above consideration, MOFs as the precursor for synthetic C-N materials which can protect the metal nanoparticles from leaching and aggregating.^[16] Herein, our group synthesized different core@shell (Co@NC) nanoparticles using ZIF-67,^[17] ZIF-67@ZIF-8 and ZIF-8@ZIF-67 as sacrificial templates: (a) the core@shell loaded on hollow nitrogen doped carbon polyhedron (HNC) (Co@NC/HNC), (b) the core@shell dispersed on the inner face of HNC (Co@NC), and (c) core@shell encapsulated in nitrogen doped carbon tube dispersed on the HNC (Co@NCT/HNC) catalysts, respectively. It is interesting to found that the thermal converted ZIF-67 and ZIF-67@ZIF-8 maintain their octahedral morphology with Co nanoparticles dispersed uniformly on the outer or inner surface. However, the converted ZIF-8@ZIF-67, produces NCT/HNC only under the same conditions. The ICP-AES analysis indicates that the Co loadings are 32.10, 12.37, and 9.81% (Table S1), respectively. Here, Co nanoparticles were encapsulated in the nitrogen doped NCT which grow on the HNC. More importantly, the NCTs are expected to improve the rate of hydrogen transfer to the substrate surface during the hydrogenation reaction. It is worth noting that the proper surface area of the materials will also accelerate the hydrogenation catalytic performance. As expected, Co@NCT/HNC exhibits higher hydrogen evolution than that of AB and superior selective hydrogenation of quinoline in water/ethanol media under mild condition.



Scheme 1. The graphic scheme to illustrate the synthesis of Co-based catalysts.

The fabrication process of Co@NCT/HNC is illustrated in Scheme 1 and described detailedly in the Supporting Information. The crystalline phase and morphology of the Co@NCT/HNC were studied by powder X-ray diffraction (PXRD) and electron microscopy (SEM and TEM), respectively. PXRD pattern of Co@NCT/HNC exposes series of 2theta peaks at 44.2°, 51.5°, and 75.8° assigned to the planes (111), (200), and (220) of Co (JCPDS No. 15-0806) and a broad peak at *ac.* 26° assigned to graphitic carbon. The component of Co nanoparticle was confirmed by X-ray photoelectron spectroscopy (XPS) measurements (Figure 2a-c), in which the Co 2p exhibits two broad peaks at 777.7 (778.2) and 792.8 (793.3) eV, corresponding to Co 2p_{3/2} and 2p_{1/2}, respectively. Their separation is 15.1 eV which is similar to Co nanoparticle. Furthermore, Figure 2c shows the N 1s XPS spectrum for the catalyst, which can be fitted into three sub peaks (pyridinic N, 397.9 eV; pyrrolic N, 400.2 eV; Graphitic N, 401.4 eV). In other word, the existence of C-N-H implies substantial N-H groups decorated on the surface of NCTs which can create defects in the NCTs matrix confirmed by Raman spectrum (Figure S6 and S7). In addition, the C1s spectrum confirms the existence of C-C (284.5 eV) and C-N (285.1 eV), indicating the successful doping of N into carbon tubes.

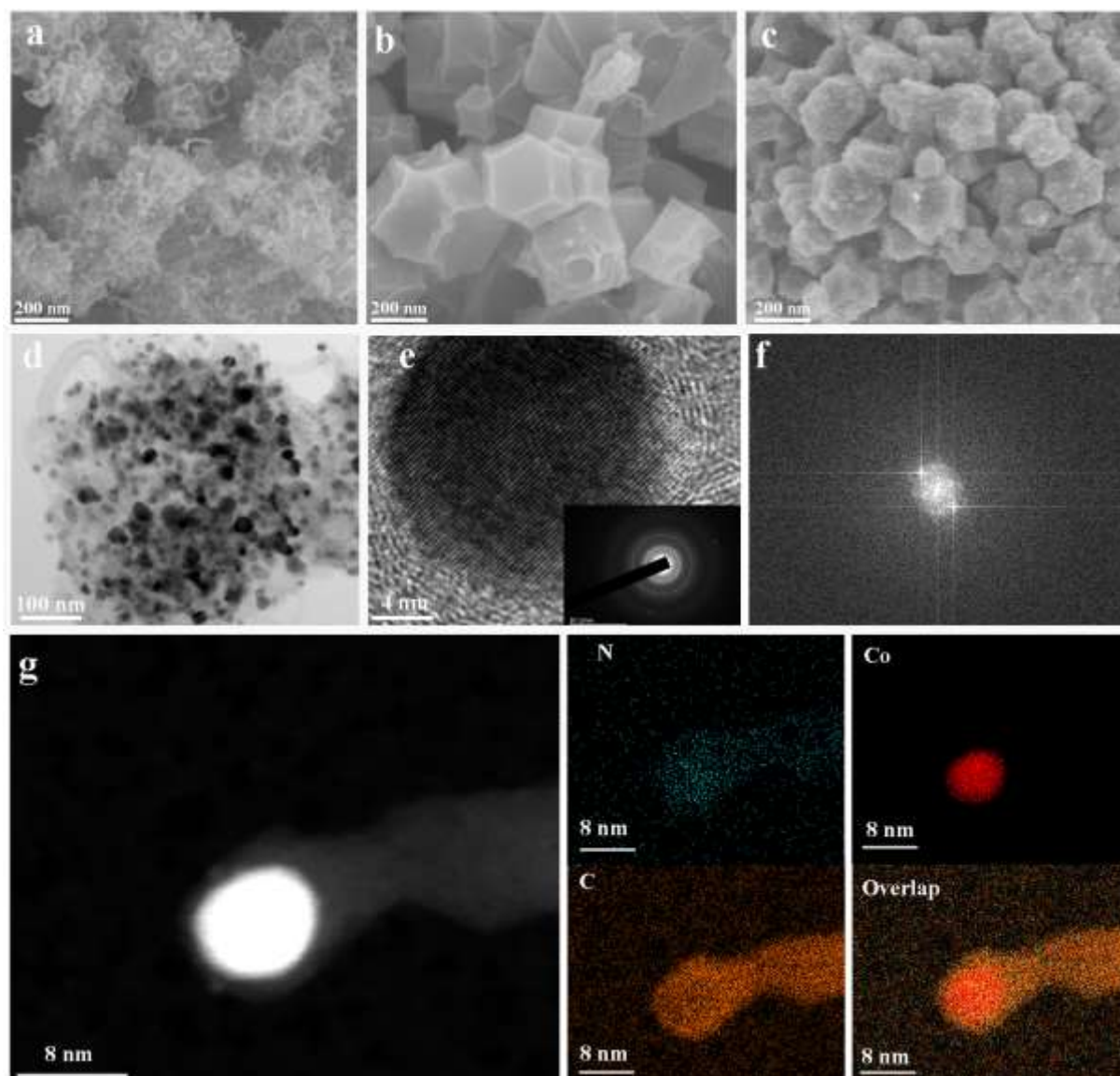


Figure 1. a, b, c) SEM images of Co@NCT/HNC, Co@NC and Co@NC/HNC, respectively. d) and e) the high-resolution STEM. f) the corresponding FFT images of Co@NCT/HNC. g) EDS elemental mapping of C, N, and Co.

As shown in Figure 1a-c, SEM and TEM images shown in Figure 1a, b, and c, indicated that the Co@NCT/HNC pyrolysed by ZIF-8@ZIF-67 is typical of carbon tube dispersed on HNC, while Co@NC obtained by pyrolysis of ZIF-67@ZIF-8 is characteristic of Co@NC core-shell nanoparticles dispersed inner face of the HNC. The surface of the hollow nitrogen-doped framework is smooth (Figure 1b). Co@NC/HNC derived from the pyrolysis of ZIF-67 is corresponding to the Co@NC nanoparticles that dispersed on the outer surface of the HNC. For getting more structural details, high-angle annular dark-field scanning transmission

electron microscopy (HAADF-STEM) images were collected, and which reveal bamboo-like carbon nanotubes with the average diameter of about 6 nm. The transparent NCTs and the “knots” of Co nanoparticle indicate that the wall is very thin. Although almost Co NPs are encapsulated in tips of the nanotubes, some of them are still embedded in the middle of nanotubes. These evidence suggest the growth and graphitization mechanism of NCTs in terms of the catalysis.^[18] Furthermore, EDS elemental mapping measurement Co, N, and C elements in the entire architecture (Figure 1g), which is in good consistent with the XPS curves. Remarkably, the N element not only disperses on NCTs, but also concentrates more around the encapsulated Co particles, reflecting the unique structure of Co@NC confined in the NCTs which dispersed on the HNC models.

To further explore the local atomic structures of the Co nanoparticle, X-ray absorption fine structure (XAFS) spectra at Co K-edge were carried (Figure 2d). Both Co K-edge $k^3\chi(k)$ oscillation curve (Figure 2e) and corresponding Fourier transform (FT) curve for Co@NCT/HNC were found to the same as the pure Co nanocrystal, indicating the Co mainly existed in the form of Co nanoparticle. However, the Co K-edge XANES of Co@NCT/HNC is very distinct compared with those of the Co foil, CoO and Co₃O₄. The energy absorption threshold value for Co@NCT/HNC was located with the Co foil, indicating that the sample has same valent state with Co. The white line of Co K-edge XANES of sample has more intensity than the Co foil (Figure 2f), suggesting that the surfaced Co atoms have very strong influence to the carbon tube. The surface areas and pore size of Co@NCT/HNC, Co@NC and Co@NC/HNC were determined by N₂ adsorption measurements (Figure S5), in which Co@NCT/HNC exhibits a moderate surface area of 325.4 m² g⁻¹. In addition, an obvious hysteresis loop occurred in the N₂ adsorption-desorption isotherm, which is a typical characteristic of mesoporous materials. Therefore, the synergetic factor of moderate surface area and the encapsulated Co NPs, may boost the catalysis for hydrogen evolution from hydrogenation reaction.

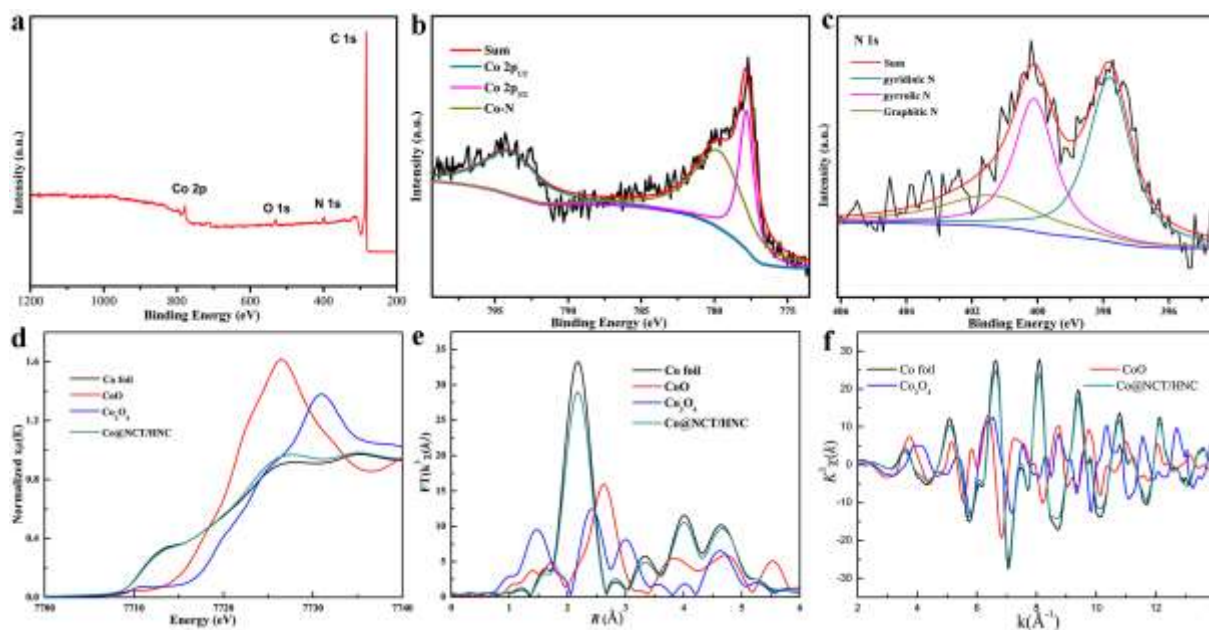


Figure 2. a) the XPS survey of Co@NCT/HNC, b) Co 2p and c) N 1s. d) XANES of Co@NCT/HNC, CoO, Co₃O₄, and Co foil. e) FT at R space and k space. f) WT of the Co K-edge.

To explore the catalytic properties of Co@NCT/HNC, we selected the hydrogenation of the benchmark substrate quinoline as a model reaction. Pleasingly, the evolution of the reactant and product distributions with reaction time revealed that quinoline can be smoothly converted into py-THQ without by-product under mild conditions and friend solvent of water (Figure 3c). A quantitative yield of py-THQ was obtained in 2 hours. The performance of Co@NCT/HNC is better than the other reported metal catalysts (Table S2). The high activity and selectivity of the catalyst make it possible for feasible applications. Furthermore, the reaction conditions were optimized for the hydrogenation of quinoline through variation of hydrogen resource and temperature, however, the quinoline has not hydrogenated when the hydrogen resource has been changed to NaBH₄ or hydrazine hydrate. The catalytic activity of the catalyst is insensitive to reaction temperature, the conversion and the selectivity without declined when the temperature within the range of 60-100 °C. Due to the support of the internal ZIF-8, ZIF-67 of the shell layer does not aggregate during the pyrolysis process, which increases the dispersion of the metal, along with specific surface area and active sites of the material. At the same time, the hollow structure and the carbon tube on the surface

facilitate the storage and transfer of hydrogen. To verify the necessity of the Co@NCTs, we prepared the sample Co@NC deposited on the outer and inner surface of HNC for comparison (Figure 1b, c and XRD in Figure S2). Co@NC can also achieve the transformation of quinoline to py-THQ selectively. However, in terms of the conversion, Co@NC exhibited a remarkable lower activity which are 29.2 and 78.6% (Figure 3b), respectively. Furthermore, to better understand the results, the AB hydrolysis catalyzed by various catalysts has been studied. We can see from Figure 3a, Co@NCT/HNC exhibits the best hydrolysis performance.

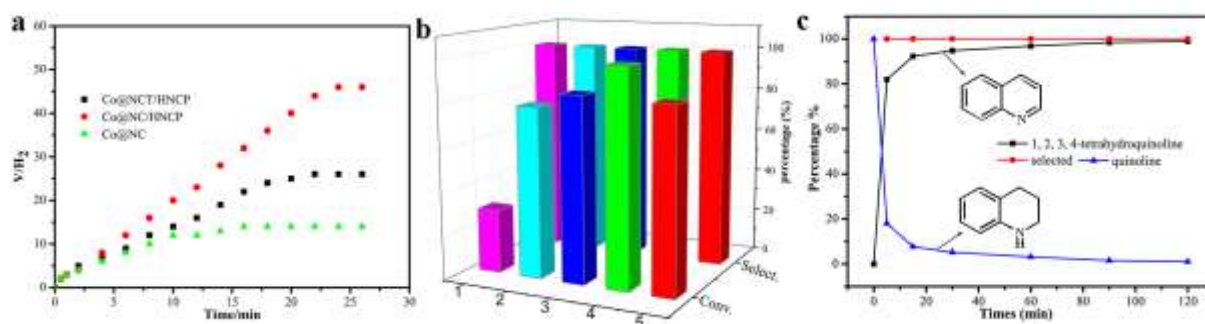
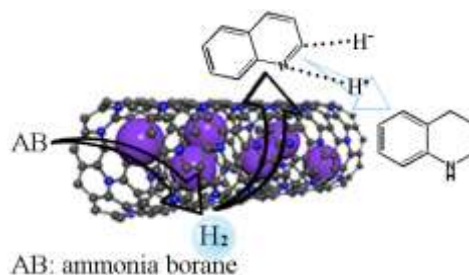


Figure 3. a) The AB hydrolysis reaction catalyzed by various catalysts. b) The performance of hydrogenation of quinolines with different catalysts (1: Co@NC/HNC; 2: Co@NC; 3-5: Co@NCT/HNC with different pyrolysis times). c) Kinetic curves and selectivity for quinoline hydrogenation with Co@NCT/HNC (reaction conditions: with 1.3% mmol catalyst dispersed in 10 mL deionized water and 5 mL ethanol, under 65 °C).

With the catalytic mechanism in mind, we conjecture a possible mechanism for the hydrogenation of quinoline over Co@NCT/HNC. We propose a reaction mechanism for the catalysis (scheme 2), the hydrogen produced by hydrolysis of ammonia borane firstly transfer to the surface of Co particles and then be cleaved to H^- and H^+ . Meanwhile, the substrates enriched in the hollow structure are ready to be hydrogenated by the hydrogen species which produce the py-THQ.



Scheme 2. Possible pathway for the hydrogenation of quinoline over Co@NCT/HNC.

Subsequently, considering the superb activity of the catalyst, the substituted quinoline with different groups have been chosen as expanded substrates to assess the active of the catalyst for the hydrogenation of N-hetero cyclic compounds. The results have been listed in Table 1, which show that Co@NCT/HNC has extremely activity and chemo-selectivity on the reduction of all the expanded substrates whatever they are electro-withdrawing groups or electron-donating groups.

Table 1. Hydrogenation of quinolines with different substitute groups by Co@NCT/HNC.

Entry	Substrate	Temp.(°C)	Time(h)	Product	Conv.(%)	Selected(%)
1		45	2		99	>99
2		60	5		99	>99
3		60	5		97.5	>99
4		60	6		81	>99
5		45	5		99	>99
6		45	2		99	>99

In conclusion, we have designed and obtained high activity Co NPs catalyst encapsulated in N-doped carbon tubes which well dispersed on the hollow N-doped carbon polyhedron *via* the approach of step by step self-assembly and confined pyrolysis. The produced catalyst demonstrated high activity of hydrogenation of quinoline with high chemo selective by

hydrogen evolution from ammonia borane. The admirable catalytic performance can be attributed to the followings: (a) the size distribution of the catalyst is smaller (*ac.* 8 nm) which can make the active sites exposed to the substrate; (b) the hollow structure and the carbon tube on the surface facilitate the transfer of hydrogen to the surface of the reactant; (c) the moderate surface area and the mesoporous pores allow the facile approaching of catalytic active sites; (d) the N-doped structures provide a protection which greatly weakening the strong coordination between N-heteroarenes and Co NPs; (e) the NCTs' encapsulation structure can enormously reduce the extent of leaching and prevent the Co NPs aggregating. The achieved success in the encapsulation of Co NPs within NCTs dispersed on the surface of HNC may pave the way for designing highly active and reusable catalysts for hydrogenating more challenging molecules by hydrolysis of ammonia borane.

Acknowledgements

Our work was funded by the National Natural Science Foundation of China (nos. 21401004, 21571092, 21973029), the Natural Science Foundation of Anhui Province (nos. 1508085QB36), and National Creative Plan of Students (201810370443), the Open Foundation of Anhui Laboratory of Molecule-based Materials (fzj19005).

References

- [1] a) R. M. Bullock, *Science* **2013**, *342*, 1054; b) P. Etayoa, A. Vidal-Ferran, *Chem. Soc. Rev.* **2013**, *42*, 728; c) R. V. Jagadeesh, A.-E. Surkus, H. Junge, M.-M. Pohl, J. Radnik, J. Rabeah, H. Huan, V. Schuemann, A. Bruckner, M. Beller, *Science* **2013**, *342*, 1073; d) P. J. Chirik, *Acc. Chem. Res.* **2015**, *48*, 1687; e) J. Huang, F. Cheng, B. P. Binks, H. Yang, *J. Am. Chem. Soc.*, **2015**, *137*, 15015; f) S. X. Bai, L. Z. Bu, Q. Shao, X. Zhu, X. Q. Huang, *J. Am. Chem. Soc.* **2018**, *140*, 8834.
- [2] a) D. S. Wang, Q. A. Chen, S. M. Lu and Y. G. Zhou, *Chem. Rev.*, **2012**, *112*, 2557; b) V. Sridharan, P. A. Suryavanshi, J. C. Menéndez, *Chem. Rev.* **2011**, *111*, 7157.
- [3] a) D. Ge, L. Hu, J. Wang, X. Li, F. Qi, J. Lu, X. Cao, H. Gu, *ChemCatChem*, **2013**, *5*, 2183; b) S.

Zhang, Z. Xia, T. Ni, Z. Zhang, Y. Ma, Y. Qu, *J. Catal.* **2018**, 359, 101; c) N. Zhang, Q. Shao, X. H. Xiao, X. Q. Huang, *Adv. Funct. Mater.* 2018, 29, 1808161.

[4] a) M. Guo, C. Li, Q. Yang. *Catal. Sci. Technol.* **2017**, 7, 2221; b) Y. T. Xia, J. Ma, X. D. Wang, L. Yang, L. Wu, *Catal. Sci. Technol.* **2017**, 7, 5515; c) N. Hashimoto, Y. Takahashi, T. Hara, S. Shimazu, T. Mitsudome, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Chem. Lett.* **2010**, 39, 832; d) Y. Gong, P. Zhang, X. Xu, Li, Y.; Li, H.; Wang, Y. *J. Catal.* **2013**, 297, 272; e) M. M. Dell'Anna, V. F. Mali, M. Capodiferro, D. Manno, P. Cotugno, A. Monopoli, P. Mastrorilli, *Appl. Catal. A* **2014**, 481, 89.

[5] a) M. Fang, R. A. Sánchez-Delgado, *J. Catal.* **2014**, 311, 357; b) L. Zhang, X. Wang, Y. Xue, X. Zeng, H. Chen, R. Li, S. Wang, *Catal. Sci. Technol.* **2014**, 4, 1939; c) H. Konnerth, M. H. G. Pechtl, *Green Chem.* **2017**, 19, 2762.

[6] a) A. Karakulina, A. Gopakumar, I. Akcok, B. L. Roulier, T. LaGrange, S. A. Katsyuba, S. Das, P. J. Dyson, *Angew. Chem. Int. Ed.* **2016**, 55, 292; b) J. Wen, R. Tan, S. Liu, Q. Zhao, X. Zhang, *Chem. Sci.* **2016**, 7, 3047; c) M. N. Shaikh, M. A. Aziz, A. N. Kalanthoden, A. Helal, A. S. Hakeem, M. Bououdina, *Catal. Sci. Tech.* **2018**, 8, 4709.

[7] a) P. Barbaro, L. Gonsalvi, A. Guerriero, F. Liguori, *Green Chem.* **2012**, 14, 3211; b) Y.-G. Ji, K. Wei, T. Liu, L. Wu, W.-H. Zhang, *Adv. Synth. Catal.* **2017**, 359, 933; c) J. Wu, J. H. Barnard, Y. Zhang, D. Talwar, C. M. Robertson, J. Xiao, *Chem. Commun.* **2013**, 49, 7052.

[8] a) D. Ren, L. He, L. Yu, R.-S. Ding, Y.-M. Liu, Y. Cao, H.-Y. He, K.-N. Fan, *J. Am. Chem. Soc.* **2012**, 134, 17592; b) M. Yan, T. Jin, Q. Chen, H. E. Ho, T. Fujita, L. Y. Chen, M. Bao, M. W. Chen, N. Asao, Y. Yamamoto, *Org. Lett.* **2013**, 7, 1844.

[9] a) A. Stanislaus, B. H. Cooper, *Catal. Rev.: Sci. Eng.* **1994**, 36, 75; b) X. Wang, W. Chen, L. Zhang, T. Yao, W. Liu, Y. Lin, H. Ju, J. Dong, L. Zheng, W. Yan, X. Zheng, Z. Li, X. Wang, J. Yang, D. He, Y. Wang, Z. Deng, Y. Wu, Y. Li, *J. Am. Chem. Soc.* **2017**, 139, 9419.

[10] a) X. Liu, S. Li, Y. Liu, Y. Cao, *Chin. J. Catal.* **2015**, 36, 1461; b) F. Jin, J. Yun, G. Li, A. Kishita, K. Tohji, H. Enomoto, *Green Chem.* 2008, 10, 612.

[11] a) F. H. Stephens, V. Pons, R. T. Baker, *Dalton Trans.* **2007**, 2613; b) Q. L. Zhu, Q. Xu, *Energy Environ. Sci.* **2015**, 8, 478; c) C. W. Hamilton, R. T. Baker, A. Staubitz, I. Manners, *Chem. Soc. Rev.* **2009**, 38, 279.

[12] S. Chakraborty, W. W. Brennessel, W. D. Jones, *J. Am. Chem. Soc.* **2014**, 136, 8564.

- [13] a) I. Sorribes, L. Liu, A. Doménech-Carbó, A. Corma, *ACS Catal.* **2018**, *8*, 4545; b) G. Li, H. Yang, H. Zhang, Z. Qi, M. Chen, W. Hu, L. Tian, R. Nie, W. Huang, *ACS Catal.* **2018**, *8*, 8396; c) R. Adam, J. R. Cabrero-Antonino, A. Spannenberg, K. Junge, R. Jackstell, M. Beller, *Angew. Chem., Int. Ed.* **2017**, *56*, 3216; d) Z. Wei, Y. Chen, J. Wang, D. Su, M. Tang, S. Mao, Y. Wang, *ACS Catal.* **2016**, *6*, 5816; e) M. Tang, J. Deng, M. Li, X. Li, H. Li, Z. Chen, Y. Wang, *Green Chem.* **2016**, *18*, 6082.
- [14] a) E. K. Rideal, *J. Chem. Soc.* **1951**, 1640; b) N. Zhang, Q. Shao, P. T. Wang, X. Zhu, X. Q. Huang, *Small*, **2018**, *14*, 1704318; c) P. T. Wang, Q. Shao, X. N. Cui, X. Zhu, X. Q. Huang, *Adv. Funct. Mater.* **2018**, *28*, 1705918.
- [15] a) C. Bai, A. Li, X. Yao, H. Liu, Y. Li, *Green Chem.* **2016**, *18*, 1061; b) R. R. Yun, S. Zhang, W. J. Ma, X. Lv, S. J. Liu, T. Sheng, S. N. Wang, *Inorg. Chem.* **2019**, *58*, 9469; c) R. R. Yun, W. J. Ma, S. N. Wang, W. G. Jia, B. S. Zheng, *Inorg. Chem.* **2019**, *58*, 6137.
- [16] a) G. Lu, S. Li, Z. Guo, O. K. Farha, B. G. Hauser, X. Qi, Y. Wang, X. Wang, S. Han, X. Liu, J. S. DuChene, H. Zhang, Q. Zhang, X. Chen, J. Ma, S. C. J. Loo, W. D. Wei, Y. Yang, J. T. Hupp, F. Huo, *Nat. Chem.* **2012**, *4*, 310; b) K. Shen, X. Chen, J. Chen, Y. Li, *ACS Catal.* **2016**, *6*, 5887; c) R. R. Yun, L. R. Hong, W. J. Ma, W. G. Jia, S. J. Liu, B. S. Zheng, *ChemCatChem*, **2019**, *11*, 724; d) Y. Chen, Z. Wang, S. Mao, Y. Wang, *Chin. J. Catal.* **2019**, *40*, 971; e) Y. Cao, S. Mao, M. Li, Y. Chen, Y. Wang, *ACS Catal.* **2017**, *7*, 8090.
- [17] a) H. Hayashi, A. P. Côté, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Nat. Mater.* **2007**, *6*, 501; b) J. Yang, F. Zhang, H. Lu, X. Hong, H. L. Jiang, Y. E. Wu, Y. D. Li, *Angew. Chem. Int. Ed.* **2015**, *54*, 10889; c) X. Wang, W. Chen, L. Zhang, T. Yao, W. Liu, Y. Lin, H. Ju, J. Dong, L. Zheng, W. Yan, X. Zheng, Z. Li, X. Wang, J. Yang, D. He, Y. Wang, Z. Deng, Y. E. Wu, Y. D. Li, *J. Am. Chem. Soc.* **2017**, *139*, 9419; d) J. Wang, W. Liu, G. Luo, Z. Li, C. Zhao, H. Zhang, M. Zhu, Q. Xu, X. Wang, C. Zhao, Y. Qu, Z. Yang, T. Yao, Y. Li, Y. Lin, Y. E. Wu, Y. D. Li, *Energy Environ. Sci.* **2018**, *11*, 3375.
- [18] a) T. Cao, D. Wang, J. Zhang, C. Cao, Y. Li, *Chem.-Eur. J.* **2015**, *21*, 14022; b) W. Yang, X. Liu, X. Yue, J. Jia, S. Guo, *J. Am. Chem. Soc.* **2015**, *137*, 1436; c) Y. Guo, P. Yuan, J. Zhang, H. Xia, F. Cheng, M. Zhou, J. Li, Y. Qiao, S. Mu, Q. Xu, *Adv. Funct. Mater.* **2018**, 1805641.