Inorganic Chemistry

pubs.acs.org/IC

Article

# Encapsulating Cobalt into N-Doping Hollow Frameworks for Efficient Cascade Catalysis

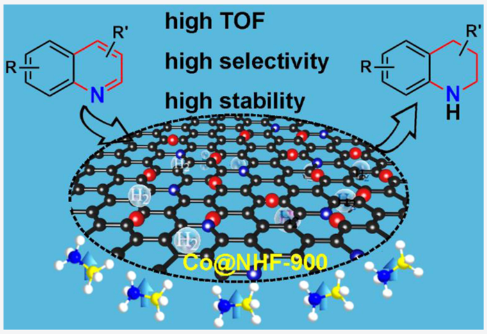
Ruirui Yun,* Beibei Zhang, Chuang Qiu, Ziwei Ma, Feiyang Zhan, Tian Sheng,* and Baishu Zheng*

Cite This: *Inorg. Chem.* 2021, 60, 9757−9761

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

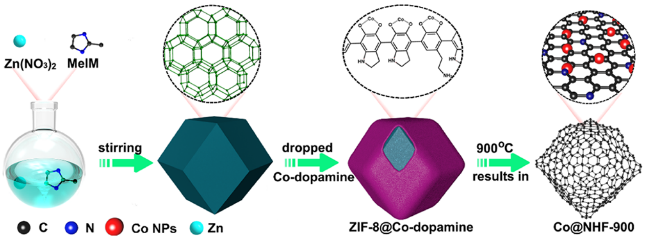
**ABSTRACT:** The development of nonprecious catalysts for hydrogenation of organic molecules is of great importance in heterogeneous catalysis. Herein, we report a series of N-doped hollow carbon frameworks encompassing cobalt nanoparticles (denoted as Co@NHF-900) constructed as a new kind of reusable catalyst for this purpose by pyrolysis of ZIF-8@Co−dopamine under Ar atmospheres. Notably, the framework of ZIF-8 is essential for efficient catalyst by providing a carbon framework to support Co−dopamine. The experimental results reveal that the ZIF-8 renders a large hollow place within the catalysts, allowing the enrichment of the substrate and windows of the hollow structure and the ease of mass transfer of products during the reaction. All of the virtues made Co@NHF-900 a good candidate for hydrogenation of quinolines with high activity (TOF value of 119 $h^{-1}$, which is several times than that of akin catalysts) and chemoselectivity.



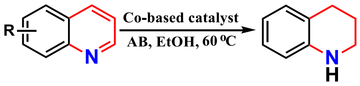
## ■ INTRODUCTION

In view of many byproducts generated during the chemical synthesis process, developing a high-performance catalytic system is of great demand and arouses wide attention.[1−3] Consequently, there is an urgent need to design and synthesize catalysts with high activity and selectivity.[4−6] In this regard, the non-noble metal catalysts, such as Fe- and Co-based materials, have attracted enormous interest due to their low cost and high selectivity in comparison to the precious metal-based catalysts.[7−10] Nowadays, unremitting efforts have been devoted to selective hydrogenation reactions using inexpensive metal-based catalysts.[11,12] Especially, the selective hydrogenation of azacyclo compounds with heterogeneous cobalt or other metal-based catalysts using $H_2$ as well as alternative transfer hydrogen resources has been studied. This priority of the heterogeneous catalytic system is because the heterogeneous catalysts can be easily separated from the reaction system, although the structure of the catalysts is ambiguous to precisely recognize at atomic levels.[13,14] Well-dispersed non-noble metal nanoparticles supported by nitrogen-doped porous carbon have attracted growing interest due to their well confirmable structure.[15−17]

### Scheme 1. Graphical Illustration of the Synthesis of Co@NHF-900



### Table 1. Activity of Hydrogenation of Quinoline with Different Co-Based Catalysts[a]

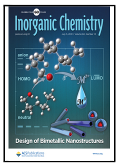


| entries | catalysts | conv. (%) | select. (%) |
|---|---|---|---|
| 1 | $Co_{ac}$@NHF-900 | <65 | >99 |
| 2 | Co@NHF-700 | 0 | >99 |
| 3 | Co@NHF-800 | 0 | >99 |
| 4 | Co@NHF-900 | >99 | >99 |

[a] Reaction conditions: 0.2 mmol quinoline, 1 mmol AB (named ammonia borane), 5 mg of a catalyst, 15 mL of a solvent (EtOH/$H_2O$; 1:2), 60 °C, 2 h. Conversions are determined by gas chromatography−mass spectrometry (GC-MS) using *n*-hexadecane as the standard.

As a specifically valuable building unit in synthetic bioactive compounds, 1,2,3,4-tetrahydroquinoline (THQ) has mounts of applications in agrochemicals, drugs, and biomolecules.[18,19] Moreover, the atom-efficient methodology to obtain THQ often

**Received:** April 6, 2021
**Published:** June 11, 2021



ACS Publications

https://doi.org/10.1021/acs.inorgchem.1c01063

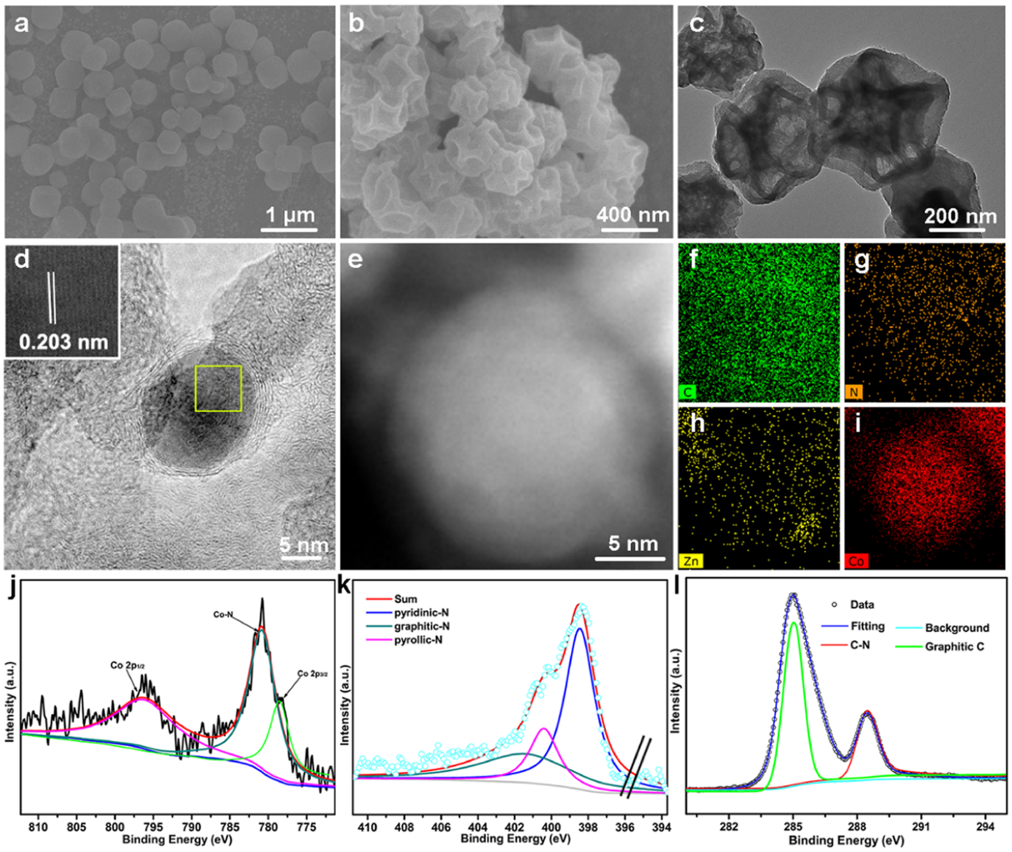


**Figure 1.** (a and b) SEM images of Co−dapamine@ZIF-8 and Co@NHF-900, respectively; (c and d) TEM and high-resolution TEM images of Co@NHF-900; (e−i) energy-dispersive system (EDS) mapping of Co@NHF-900; and (j−l) XPS spectra of Co, N, and C of Co@NHF-900, respectively.

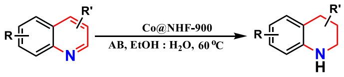
uses the hydrogenation of quinoline; the reduction process, however, is still challenging due to the catalyst deactivation, which was caused by the easy combination between the metal centers and the nitrogen atoms in the quinoline molecule or its other reduced products.[20−22] Although various heterogeneous catalysts have been successfully developed, this reduction still depends on the noble metal-based catalysts. Hence, designing nonprecious metal-based catalysts with high activity and selectivity for the hydrogenation of quinolines under milder conditions is essential.

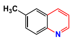
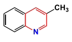
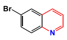
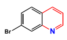
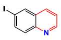
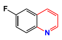
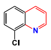
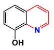
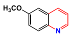
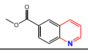
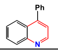
Zeolitic imidazolate frameworks (ZIFs) possess high porosity that can enrich a substrate to increase the collision probability of reactants,[23−25] which has been selected as the template to synthesize the carbon-supported catalysts and is extremely attractive in recent years.[26−28] As a typical example, the nanoparticles obtained by pyrolysis of ZIF-8 and ZIF-67 show less catalytic activity toward hydrogenation reactions. Taking the above reasons in account and considering our previous work,[29−31] here, we synthesized N-doping hollow graphitic carbon-supported Co core−shell nanoparticles (named Co@NHF-900) by encapsulating ZIF-8 in the cobalt−dopamine and subsequent pyrolysis, which is described in Scheme 1. All of the as-synthesized samples were tested for the liquid-phase hydrogenation of quinoline at 60 °C. Catalytic experiments exhibit that Co@NHF-900 possesses the highest activity and selectivity, which allows the overall conversion into the target product, THQ in 99%. Obviously, the pyrolysis temperature and the cobalt salts strongly influence the catalytic performance: the materials have the highest activity at the calcined temperature of 900 °C, and the conversion reduces to 65% with the cobalt nitrate being replaced by Co(III) acetylacetonate (denoted as $Co_{ac}$@NHF-900) (Table 1).

## ■ RESULTS AND DISCUSSION

To investigate the superb activity and selectivity of Co@NHF-900, the characterization of its structure was carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM), high-

**Table 2. Reduction of Quinoline Derivatives by Co@NHF-900**[a]



| Entry | Substrate | Time (h ) | Conv./select. (%) | Entry | Substrate | Time (h) | Conv./select. (%) |
|---|---|---|---|---|---|---|---|
| 1 |  | 2 | >99 | 2 |  | 2 | >99 |
| 3 |  | 2 | >99 | 4 |  | 2 | >99 |
| 5 |  | 2 | >99 | 6 |  | 3 | ~95 |
| 7 |  | 2 | >99 | 8 |  | 2 | >99 |
| 9 |  | 2 | >99 | 10 |  | 2 | >99 |
| 11 |  | 2 | >99 | 12 |  | 2 | >99 |

[a]Note: reaction conditions are the same as presented in Table 1.

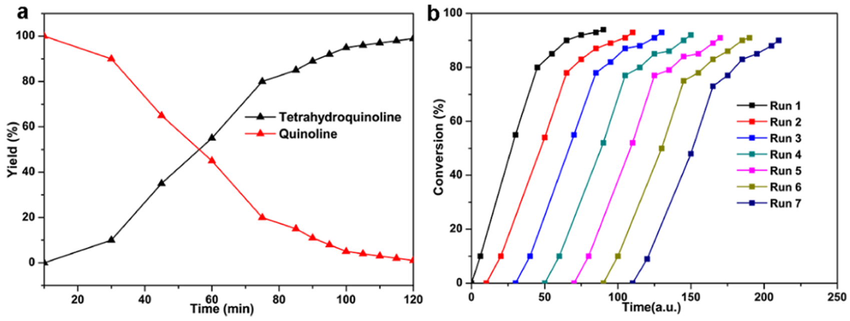


**Figure 2.** (a) Kinetic curves for hydrogenation of quinoline with Co@NHF-900 (reaction conditions: with 5 mg of catalyst and 0.2 mmol substrate dispersed in 15 mL of solution at 60 °C). (b) Reusability tests of the optimal catalyst.

resolution transmission electron microscopy (HRTEM), Brunauer−Emmett−Teller (BET) techniques, and X-ray photoelectron spectroscopy (XPS). The XRD patterns show that Co@NHF-900 exhibits cobalt phase with the PDF card no. 15-0806; however, in the case of $Co_{ac}$@NHF-900, XRD patterns show the presence of both metallic and oxide cobalt phases (Co and CoO, Figure S2) which may cause the decrease in the activity. Therefore the high activity may be attributed to Co NPs. Compared with the other catalysts, Co@NHF-900 shows larger BET surface areas of 730 $m^2/g$ (Figure S4, Co@NHF-700 and Co@NHF-800 show 414 and 467 $m^2/g$, respectively), which causes concentration enrichment of the substrate to enhance the catalysis process. More importantly, the large pore size of the catalyst also exposes more active site to facilitate the catalysis process.

There is a large cave of the carbon framework as a result of the pyrolysis of ZIF-8, as shown in Figure 1a−c, and there are no obviously big particles on the surface of the polyhedral framework. Furthermore, the HRTEM analysis of the catalyst reveals that the particle size of Co@NHF-900 is in the range of *ac.* 8−10 nm; most of the particles were encapsulated in N-doped carbon to form a core−shell structure (Figure 1d,e), and all elements are scattered well (Figure 1f−i). Moreover, XPS analysis was performed to confirm the nature of Co species of the active catalyst (Figure 1j−l). Peaks observed at 778.48, 780.85, and 796.39 eV corresponded to $Co^0$ and Co−N species, which illustrates that the metal particles were anchored on the inner surface of the shell through coordinated bonds.[32,33] In addition, a series of peaks appear at 398.47, 400.40, and 401.57 eV, indicating the presence of pyridinic N and graphitic N in the N-doping graphitic carbon framework.[34]

Considering the successful catalysis for hydrogenation of quinoline, the catalyst was used for the derivatives of quinoline with different functional groups, which are listed in Table 2. It is noteworthy that the derivatives with both electron-withdrawing and electron-donating groups are hydrogenated to obtain the corresponding products with a high conversion of up to 99% and without alkyl group removal and dehalogenation (entries 1−9). Interestingly, although there are competitive unsaturated groups, the catalyst still shows outstanding activity and excellent selectivity (entries 10 and 12). The extreme results highlight the activity and its eminent virtues compared with those of noble metal catalysts in the process of hydrogenation of quinolines.

A time-dependent experiment of reduction of quinoline with an optimal catalyst and using ammonia borane as the hydrogen resource was used to conduct the reaction kinetic investigation (Figure 2a). The kinetic curve indicates that the conversion is fast within the first hour and without any byproducts. To further prove the practicability of the optimal catalyst, its stability and recyclability have been tested. As shown in Figure 2b, due to the N-doping carbon shell, the metal core as the active site can be protected from etching and aggregating, leading to Co@NHF-900 having good recyclability, which can be reused at least seven times without any loss in the conversion. More interestingly, the catalyst can be separated easily from the reaction medium by the magnetism of the nature of the catalyst, which solves the problem that catalysts are hard to separate during the catalysis process in the practical industry.

## ■ CONCLUSIONS

In summary, a hollow N-doping carbon framework supported core−shell catalyst of Co@NHF-900 has been designed and constructed by template synthesis of the Co−dopamine coating on the ZIF-8 and subsequent pyrolysis. It was evidenced that the catalyst shows excellent performance for hydrogenation of quinolines due to the large surface areas of the carbon framework, which facilitates substrate enrichment and transfer, and the well-distributed Co particles, which provide uniform active sites. Meanwhile, the Co-based catalyst can be separated easily by magnetism and reused at least seven times due to the carbon shell that well protects the nanoparticles from leaching in the solvent. This work paves a new path to design hollow structures with uniformly distributed nanoparticles and promotes the performance of heterogeneous catalytic reactions.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c01063.

Experimental section; characterization (Figures S1−S5); and gas chromatography graph (Table S1) (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Authors

**Ruirui Yun** − *The Key Laboratory of Functional Molecular Solids, Ministry of Education, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 214001, P. R. China;* orcid.org/0000-0002-5598-5076;
Email: ruirui58@ahnu.edu.cn

**Tian Sheng** − *The Key Laboratory of Functional Molecular Solids, Ministry of Education, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 214001, P. R. China;* orcid.org/0000-0001-5711-3012;
Email: tsheng@ahnu.edu.cn

**Baishu Zheng** − *Key Laboratory of Theoretical Chemistry and Molecular Simulation of Ministry of Education, School of*

*Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201, P. R. China;* orcid.org/0000-0002-2974-6143; Email: zbaishu@163.com

### Authors

**Beibei Zhang** − *The Key Laboratory of Functional Molecular Solids, Ministry of Education, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 214001, P. R. China*

**Chuang Qiu** − *The Key Laboratory of Functional Molecular Solids, Ministry of Education, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 214001, P. R. China*

**Ziwei Ma** − *The Key Laboratory of Functional Molecular Solids, Ministry of Education, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 214001, P. R. China*

**Feiyang Zhan** − *The Key Laboratory of Functional Molecular Solids, Ministry of Education, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 214001, P. R. China*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.inorgchem.1c01063

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was funded by the NSFC (Grant nos. 21401004 and 21973029), the Natural Science Foundation of Anhui Province (Grant nos. 1508085QB36, 1908085QB58, and 2008085MB52), and the Open Foundation of Anhui Laboratory of Molecule-Based Materials (fzj19005).

## ■ REFERENCES

(1) Meemken, F.; Baiker, A. Recent Progress in Heterogeneous Asymmetric Hydrogenation of C═O and C═C Bonds on Supported Noble Metal Catalysts. *Chem. Rev.* **2017**, *117*, 11522−11569.

(2) Liu, L. C.; Corma, A. Metal Catalysts for Heterogeneous Catalysis: From Single Atoms to Nanoclusters and Nanoparticles. *Chem. Rev.* **2018**, *118*, 4981−5079.

(3) Murugesan, K.; Senthamarai, T.; Chandrashekhar, V. G.; Natte, K.; Kamer, P. C. J.; Beller, M.; Jagadeesh, R. V. Catalytic Reductive Aminations Using Molecular Hydrogen for Synthesis of Different Kinds of Amines. *Chem. Soc. Rev.* **2020**, *49*, 6273−6328.

(4) Yang, D.; Gaggioli, C. A.; Conley, E.; Babucci, M.; Gagliardi, L.; Gates, B. C. Synthesis and Characterization of Tetrairidium Clusters in the Metal Organic Framework UiO-67: Catalyst for Ethylene Hydrogenation. *J. Catal.* **2020**, *382*, 165−172.

(5) Kim, U. B.; Jung, D. J.; Jeon, H. J.; Rathwell, K.; Lee, S. G. Synergistic Dual Transition Metal Catalysis. *Chem. Rev.* **2020**, *120*, 13382−13433.

(6) Dong, Q. B.; Zhang, X.; Liu, S.; Lin, R. B.; Guo, Y. N.; Ma, Y. S.; Yonezu, A.; Krishna, R.; Liu, G. P.; Duan, J. G.; Matsuda, R.; Jin, W. Q.; Chen, B. L. Tuning Gate-Opening of a Flexible Metal-Organic Framework for Ternary Gas Sieving Separation. *Angew. Chem., Int. Ed.* **2020**, *59*, 22756−22762.

(7) Nakatsuji, M.; Fujita, M.; Okamoto, Y.; Sugimura, T. Kinetic Analysis of the Asymmetric Hydrogenation of (E)-2,3-diphenylpropenoic Acid over Cinchonidine Derivative-modified Pd/C: Quinoline Ring Modification. *Catal. Sci. Technol.* **2020**, *10*, 6573−6582.

(8) Chen, Y. Z.; Xu, Q.; Yu, S. H.; Jiang, H.-L. Tiny Pd@Co Core-Shell Nanoparticles Confined inside a Metal-Organic Framework for Highly Efficient Catalysis. *Small* **2015**, *11*, 71−76.

(9) Yun, R. R.; Hong, L. R.; Ma, W. J.; Jia, W. G.; Liu, S. J.; Zheng, B. S. Fe/$Fe_2O_3$@N-dopped Porous Carbon: A High-Performance Catalyst for Selective Hydrogenation of Nitro Compounds. *ChemCatChem* **2019**, *11*, 724−728.

(10) Qi, L.; Chen, J. W.; Zhang, B. Y.; Nie, R. F.; Qi, Z. Y.; Kobayashi, T.; Bao, Z. B.; Yang, Q. W.; Ren, Q. L.; Sun, Q.; Zhang, Z. G.; Huang, W. Y. Deciphering a Reaction Network for the Switchable Production of Tetrahydroquinoline or Quinoline with MOF-Supported Pd Tandem Catalysts. *Acs Catal.* **2020**, *10*, 5707−5714.

(11) Murugesan, K.; Chandrashekhar, V. G.; Senthamarai, T.; Jagadeesh, R. V.; Beller, M. Reductive Amination Using Cobalt-based Nanoparticles for Synthesis of Amines. *Nat. Protoc.* **2020**, *15*, 1313−1337.

(12) Ciotonea, C.; Hammi, N.; Dhainaut, J.; Marinova, M.; Ungureanu, A.; El Kadib, A.; Michon, C.; Royer, S. Phyllosilicate-derived Nickel-cobalt Bimetallic Nanoparticles for the Catalytic Hydrogenation of Imines, Oximes and N-heteroarenes. *ChemCatChem* **2020**, *12*, 4652−4663.

(13) Yun, R. R.; Ma, W. J.; Wang, S. N.; Jia, W. G.; Zheng, B. S. High Selectivity of Hydrogenation Reaction over $Co_{0.15}$@C/PC Catalyst at Room Temperature. *Inorg. Chem.* **2019**, *58*, 6137−6142.

(14) Zhao, J. B.; Yuan, H. F.; Qin, X. M.; Tian, K.; Liu, Y. F.; Wei, C. Z.; Zhang, Z. Q.; Zhou, L. M.; Fang, S. M. Au Nanoparticles Confined in SBA-15 as a Highly Efficient and Stable Catalyst for Hydrogenation of Quinoline to 1,2,3,4-Tetrahydroquinoline. *Catal. Lett.* **2020**, *150*, 2841−2849.

(15) Pang, M. F.; Chen, J. Y.; Zhang, S. J.; Liao, R. Z.; Tung, C. H.; Wang, W. G. Controlled Partial Transfer Hydrogenation of Quinolines by Cobalt-amido Cooperative Catalysis. *Nat. Commun.* **2020**, *11*, No. 1249.

(16) Zhang, J.; Zheng, C. Y.; Zhang, M. L.; Qiu, Y. J.; Xu, Q.; Cheong, W. C.; Chen, W. X.; Zheng, L. R.; Gu, L.; Hu, Z. P.; Wang, D. S.; Li, Y. D. Controlling N-doping Type in Carbon to Boost Single-atom Site Cu Catalyzed Transfer Hydrogenation of Quinoline. *Nano. Res.* **2020**, *13*, 3082−3087.

(17) Wang, M.; Jin, Z. C.; Liu, M. J.; Jiang, G. Q.; Lu, H. B.; Zhang, Q. X.; Ju, J. F.; Tang, Y. F. Nanoplate-assembled Hierarchical Cake-like ZnO Microstructures: Solvothermal Synthesis, Characterization and Photocatalytic Properties. *RSC Adv.* **2017**, *7*, 32528−32535.

(18) Sorribes, I.; Liu, L. C.; Domenech-Carbo, A.; Corma, A. Nanolayered Cobalt-Molybdenum Sulfides as Highly Chemo- and Regioselective Catalysts for the Hydrogenation of Quinoline Derivatives. *Acs Catal.* **2018**, *8*, 4545−4557.

(19) Murugesan, K.; Chandrashekhar, V. G.; Kreyenschulte, C.; Beller, M.; Jagadeesh, R. V. A General Catalyst Based on Cobalt Core-Shell Nanoparticles for the Hydrogenation of N-Heteroarenes Including Pyridines. *Angew. Chem., Int. Ed.* **2020**, *59*, 17408−17412.

(20) Lv, Y.; Han, M. M.; Gong, W. B.; Wang, D. D.; Chen, C.; Wang, G. Z.; Zhang, H. M.; Zhao, H. J. Fe-Co Alloyed Nanoparticles Catalyzing Efficient Hydrogenation of Cinnamaldehyde to Cinnamyl Alcohol in Water. *Angew. Chem., Int. Ed.* **2020**, *59*, 23521−23526.

(21) Papa, V.; Cao, Y. X.; Spannenberg, A.; Junge, K.; Beller, M. Development of a Practical Non-noble Metal Catalyst for Hydrogenation of N-heteroarenes. *Nat. Catal.* **2020**, *3*, 135−142.

(22) Song, Q.; Wang, W. D.; Hu, X. W.; Dong, Z. P. Ru Nanoclusters Confined in Porous Organic Cages for Catalytic Hydrolysis of Ammonia Borane and Tandem Hydrogenation Reaction. *Nanoscale* **2019**, *11*, 21513−21521.

(23) Babucci, M.; Guntida, A.; Gates, B. C. Atomically Dispersed Metals on Well-Defined Supports including Zeolites and Metal-Organic Frameworks: Structure, Bonding, Reactivity, and Catalysis. *Chem. Rev.* **2020**, *120*, 11956−11985.

(24) Choe, K.; Zheng, F. B.; Wang, H.; Yuan, Y.; Zhao, W. S.; Xue, G. X.; Qiu, X. Y.; Ri, M.; Shi, X. H.; Wang, Y. L.; Li, G. D.; Tang, Z. Y. Fast and Selective Semihydrogenation of Alkynes by Palladium Nanoparticles Sandwiched in Metal-Organic Frameworks. *Angew. Chem., Int. Ed.* **2020**, *59*, 3650−3657.

(25) Dong, Q. B.; Guo, Y. N.; Cao, H. F.; Wang, S. N.; Matsuda, R.; Duan, J. G. Accelerated $C_2H_2/CO_2$ Separation by a Se-Functionalized

Porous Coordination Polymer with Low Binding Energy. *ACS Appl. Mater. Interfaces* **2020**, *12*, 3764−3772.

(26) Song, X.; Jiang, Y.; Fang, C.; Earnshaw, J.; Na, J.; Li, X. P.; Yamauchi, Y. Hollow Carbon-Based Nanoarchitectures Based on ZIF: Inward/Outward Contraction Mechanism and Beyond. *Small* **2020**, No. e2004142.

(27) Chu, C. S.; Rao, S.; Ma, Z. F.; Han, H. L. Copper and cobalt nanoparticles doped nitrogen-containing carbon frameworks derived from CuO-encapsulated ZIF-67 as high-efficiency catalyst for hydrogenation of 4-nitrophenol. *Appl. Catal., B* **2019**, *256*, No. 117792.

(28) Tian, H.; Liu, X. Y.; Dong, L. B.; Ren, X. M.; Liu, H.; Price, C. A. H.; Li, Y.; Wang, G. X.; Yang, Q. H.; Liu, J. Enhanced Hydrogenation Performance over Hollow Structured Co-CoO$_x$@N-C Capsules. *Adv. Sci.* **2019**, *6*, No. 1900807.

(29) Yun, R. R.; Zhang, S.; Ma, W. J.; Lv, X.; Liu, S. J.; Sheng, T.; Wang, S. N. Fe/Fe$_3$C Encapsulated in N-Doped Carbon Tubes: A Recyclable Catalyst for Hydrogenation with High Selectivity. *Inorg. Chem.* **2019**, *58*, 9469−9475.

(30) Yun, R. R.; Ma, W. J.; Hong, L. R.; Hu, Y.; Zhan, F. Y.; Liu, S. J.; Zheng, B. S. Ni@PC as a Atabilized Catalyst toward the Efficient Hydrogenation of Quinoline at Ambient Temperature. *Catal. Sci. Technol.* **2019**, *9*, 6669−6672.

(31) Yun, R. R.; Zhan, F. Y.; Li, N.; Zhang, B. B.; Ma, W. J.; Hong, L. R.; Sheng, T.; Du, L. T.; Zheng, B. S.; Liu, S. J. Fe Single Atoms and Fe$_2$O$_3$ Clusters Liberated from N-Doped Polyhedral Carbon for Chemoselective Hydrogenation under Mild Conditions. *ACS Appl. Mater. Interfaces* **2020**, *12*, 34122−34129.

(32) Ning, S. B.; Xu, H.; Qi, Y. H.; Song, L. Z.; Zhang, Q. Q.; Ouyang, S. X.; Ye, J. H. Microstructure Induced Thermodynamic and Kinetic Modulation to Enhance CO2 Photothermal Reduction: A Case of Atomic-Scale Dispersed Co-N Species Anchored Co@C Hybrid. *Acs Catal.* **2020**, *10*, 4726−4736.

(33) Liu, Y. J.; Zhang, D. H.; Li, X. C.; Deng, S. J.; Zhao, D.; Zhang, N.; Chen, C. Construction of Highly-dispersed and Composition-adjustable Co$_x$N in Stable Co@Co$_x$N@C Nanocomposite Catalysts via A Dual-ligand-MOF Strategy for the Selective Hydrogenation of Citral. *Appl. Surf. Sci.* **2020**, *505*, No. 144387.

(34) Wang, H. B.; Maiyalagan, T.; Wang, X. Review on Recent Progress in Nitrogen-Doped Graphene: Synthesis, Characterization, and Its Potential Applications. *Acs. Catal.* **2012**, *2*, 781−794.