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Selective reductive annulation reaction for direct synthesis of functionalized quinolines by a cobalt nanocatalyst



Key Lab of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, People's Republic of China

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1. Introduction

Quinolines constitute a class of significantly important Nheterocycles, and they are extensively distributed in functional materials, marketing drugs [1–5], biologically active agents (e.g., anti-HIV, antimalarial, and anti-inflammation,), etc [6–8]. In general, quinolines are prepared by the well-established names reactions (i.e. Doebner-von Miller [9], Skraup [10,11], Doebner [12], Combes [13], Friedländer [14–16], etc.). In recent years, various approaches have also been nicely developed to achieve the related end [17-21]. Among them, the cyclization of 2-aminoaryl carbonyls and alkynoates offers a valuable way to access ester substituted quinolines that are used frequently for the discovery of bioactive and therapeutical products [22,23]. However, the related transformations generally suffer from difficult catalyst reusability, low chemoselectivity due to the occurrence of side reactions induced by the active 2-aminoaryl carbonyls [24,25]. In this context, the search for direct and selective synthesis of ester-linked quinolines with easily available catalysts, preferably reusable ones, still remains a higly demanding goal.

As our sustained effort toward hydrogen transfer-mediated synthesis of N-heterocycles [26–28], we believe that, in the presence of a suitable hydrogen donor (HD) and catalyst, the replacement of 2-aminoaryl carbonyls with more cost-effective and stable 2-nitroaryl carbonyls would offer an appealing approach

* Corresponding author.

ABSTRACT

Due to the extensive applications of quinolines, the search for selective construction of such products has long been an attractive subject in scientific community. Herein, by developing a new N-doped ZrO₂@C supported cobalt nanomaterial, it has been successfully applied as an efficient catalyst for the reductive annulation of 2-nitroaryl carbonyls with alkynoates and alkynones. The catalytic transformation allows synthesizing a wide array of funcitonalized quinolines with the merits of broad substrate scope, good functional group tolerance, excellent hydrogen transfer selectivity, reusable earth-abundant metal catalyst, and operational simplicity. The developed chemistry paves the ways for further design of hydrogen transfer-mediated coupling reactions by developing heterogeneous catalysts with suitable supports.

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to access ester substituted guinolines. As shown in Scheme 1, the catalytic transfer hydrogenation (TH) of the nitro group of 2nitroaryl carbonyl **1** initially generates the 2-aminoaryl carbonyl 1'. Then, the hydroamination of 1' with alkynoate 2 affords enamine A. Finally, the quinoline product 3 is afforded via intramolecular nucleophilic addition (B) followed by proton-promoted dehydration.

However, it is important to note that, to achieve the above synthetic purpose, at least two challenging issues have to be addressed: (1) There should be a compatible catalyst system to ensure that, among various reducible functionalities (nitro, alkynyl, carbonyl groups) in the electron-deficient substrates (1 and 2), the transfer hydrogenation selectively occurs on the nitro group. (2) The in situ generated active 2-aminoaryl carbonyls 1' should be timely consumed up by its hydroamination (A) with alkynoates 2, thus suppressing the occurrence of undesired side reactions such as homo-condensation.

Enlightened by the capability of cobalt in reducion of unsaturated chemical bonds [29-32], we believed that the design of a suitable supported heterogeneous cobalt catalyst might offer a solution to achieve the above synthetic goal. On one hand, the cobalt metal has preferential interaction with electron-rich heteroatoms, which would result in unique transfer hydrogenation selectivity toward the nitro group among different reducible functionalities of substrates 1 and 2. On the other hand, the supporting materials or dopants introduced drastically affect the morphology and surface chemistry of the catalytic materials, thus resulting





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Scheme 1. Envisioned new synthetic protocol.

tunable catalytic activity and selectiviy [33,34]. In recent years, different heteroatoms (i.e. B, N, P, S, etc.) have been applied for the design of functional materials [35,36]. Especially, the silica is used to adjust the pore size [37–41], and the N-element could change electronic properties of supporting materials [42,43]. Based on the information, we wish herein to report the preparation of a cobalt nanocatalyst supported on nitrogen-doped ZrO₂@C by a template method, and describe, for the first time, its application in selective reductive annulation of 2-nitroaryl carbonyls with alkynoates, which offers an efficient new platform for the synthesis of functional quinolines.

2. Experimental and result analysis

2.1. Synthesis of Co/N-ZrO₂@C

The new nanomaterial was prepared by the method shown in Fig. 1. Firstly, the metal organic framework UiO-66 composing of inorganic zirconium clusters and benzenedicarboxylate (H₂BDC) bridged linkers was synthesized according to the solvothermal method [44]. Subsequently, the mixture of $Co(OAc)_2$ -4H₂O and 1,10-phenanthroline (1,10-phen) (1:2 M ratio) in EtOH was stirred at 80 °C for 1 h to generate the cobalt complex. The silica was then introduced into the above solution by *in situ* hydrolysis of the added Si(OC₂H₅)₄ (TEOS) with aqueous ammonia. After that, the dried UiO-66 was added to the above mixture and refluxed for 4 h at 80 °C. At last, the obtained composites were pyrolyzed under argon flow at 800 °C for 3 h, followed by treatment with NaOH solution to remove silica and form the cavity [45], affording the cobalt material (Co/N-ZrO₂@C; see details in the Supporting Information (SI)).

2.2. Characterization

To understand the constituent of the prepared new material accurately, X-ray diffraction (XRD) detection was carried out. Except for the characteristic peaks of zirconium dioxide (PDF No. 49-1642), no other significant peaks belonging to cobalt species are presented in the XRD spectrum of the Co/N-ZrO₂@C (Fig. S1 in the SI), which implies that the Co species are evenly dispersed or amorphous phase. The N₂ adsorption-desorption tests of Co/N-ZrO₂@C clearly exhibit a typical IV isotherm, indicating the inclusion of mesoporous structure (Fig. S2 in the SI). Moreover, the specific BET surface area is shown as 199.2 m²/g, and the



Fig. 1. Preparation of cobalt nanocatalyst.

corresponding pore size distribution is mainly concentrated at \sim 10 nm (Fig. S2 in the SI). The results also confirm that the prepared material contains the mesoporous structure.

Further, TEM, HRTEM, and EDS have been adopted to analyze the morphology of the Co/N-ZrO₂@C composites. The TEM and HRTEM images (Fig. 2a,b) revealed the as-prepared Co/N-ZrO₂@C structure remained the initial octahedral shape of UiO-66 [46]. The TEM image (Fig. 2c) and high-angle annular dark-field scanning TEM (HAADF-STEM) image (Fig. 2d) clearly showed that the cobalt species are homogenously dispersed, which is in line with the XRD test results. Meanwhile, the corresponding element mapping images (Fig. 2e, Fig. S4) also indicate that the elements of Co, Zr, N, C and O are uniformly distributed, and the Co nanoparticles are embedded in the matrix consisting of zirconia and carbon derived from the UiO-66 MOF template, which prevents cobalt nanoparticles from agglomerating during the pyrolysis process.

The surface chemistry of the as-prepared nanomaterial was subsequently analyzed by the X-ray photoelectron spectroscopy (XPS). A range of elements corresponding to Co, N, C, O, and Zr on the samples surface were detected as 2.26%, 2.58%, 59.97%, 29.52%, and 5.67%, respectively, which are in accordance with the elemental mapping results (Fig. S4 in the SI). The N 1s XPS spectrum (Fig. S5b in the SI) revealed three different signals, corresponding to Co-N (399.01 eV), graphitic N (400.8 eV), and N oxide species (403.5 eV), respectively [47,48]. Both graphitic-N and oxidized-N emanate from the calcination of uncoordinated 1,10-Phen ligand, whereas the Co-N moieties are from the calcination of Co-1,10-Phen complex [49]. Similarly, the spectra of Co 2p (Fig. 3) could be resolved into four constituents, the two characteristic peaks located at 781.9 eV and 787.1 eV are allotted to Co-N structures, while the binding energies of 797.9 eV and 803.5 eV correspond to the cobalt oxides [50–53]. The appearance of cobalt oxides are derived from partial oxidation of cobalt atoms on the surface of Co-N species, as cobalt is susceptible to air [54,55]. The XPS results manifest that the cobalt nitrides (Co-Nx) and cobalt oxides (Co-Ox) constitute the catalytically active species in the prepared materials.

To evaluate the catalytic performance of the prepared nanomaterial, it was applied to test a benchmark reaction, the reductive annulation of 2-nitrobenzaldehyde **1a** with diethyl acetylenedicarboxylate **2a**. Pleasingly, the initial test resulted in the quinoline product **3aa** in 51% yield (entry 1, table 1). Then, we evaluated various reaction parameters, including hydrogen donors, solvents,



Fig. 2. (a, b, c) TEM images of Co/N-ZrO₂@C, respectively. (d) magnified HAADF-STEM image of Co/N-ZrO₂@C. (e) the corresponding elemental mapping of Co, Zr, N and C, respectively.



Fig. 3. Co 2p XPS spectra of Co/N-ZrO₂@C.

Table 1Screening of optimal reaction conditions.



Entry	Catalyst	solvent	3aa Yield % ^b
1	Co/N-ZrO2@C	H ₂ O	51
2	Co/N-ZrO2@C	EtOH	53
3	Co/N-ZrO2@C	t-amyl alcohol	41
4	Co/N-ZrO2@C	DMSO	20
5	Co/N-ZrO2@C	HFIP	71
6	-	HFIP	NR
7	Co/N-ZrO2@C	HFIP	NR ^c
8	Co/N-ZrO2@C	HFIP	83 ^d
9	Co/N-ZrO2@C	HFIP	(5, 0) ^e
10	Co(OAc) ₂ ·4H ₂ O	HFIP	NR
11	Co/N-ZrO2@C	HFIP	NR ^f
12	Co/ZrO ₂ @C	HFIP	70
13	Co/N-Si-ZrO2@C	HFIP	65

^a Reaction conditions: Unless otherwise specified, all reactions were performed at 120 °C for 18 h under N₂ protection by using **1a** (0.25 mmol), **2a** (0.3 mmol), catalyst (6 mol %), HFIP (1.2 mL), HCOOH (3.0 eq, 0.75 mmol), Co/N-ZrO₂@C pyrolyzed at 800 °C.

^b GC yield using hexadecane as an internal standard.

^c Without HCOOH.

^d Reaction temperature: 110 °C.

^e the hydrogen sources are respect to HCOONa, and hydrogen balloon, respectively.

^f Non-pyrolyzed Co/N-ZrO₂@C. EA: ethyl acetate, HFIP: 1,1,1,3,3,3-Hexafluoro-2propanol. NR = no reaction.

temperatures and catalysts (Table 1, Table S1 in the SI). It was found that the solvents significantly affect the reaction, and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) exhibit the highest efficiency in affording product **3aa** (entries 1–5), which might be rationalized as such alcohol could serve as an efficient proton transferring shuttle [56–58]. The absence of cobalt catalyst or hydrogen donor failed to give any products (entries 6 and 7). An optimal GC yield (83%) of product **3aa** was gained when the reaction in HFIP was performed at 110 °C in the presence of 6 mol % of catalyst and HCOOH as the hydrogen donor (entry 8, standard conditions). However, the use of catalyst precursor Co(OAc)₂-4H₂O, non-pyrolyzed Co/N-ZrO₂@C showed no activity (entries 10, 11), and other hydrogen donors, non-N-doped or Si-non-etching materials using UiO-66 as the support of cobalt resulted in either no activity or low efficiency (entries 9, 12–13).

3. Practical applicability of the catalyst

With the optimal conditions established, we next got down to evaluating the universality of this catalytic scheme. Initially, a series of 2-nitrobenzaldehydes 1 in combination with alkynoate 2a (for their structures, see Scheme S1 in the SI) were examined. As shown in scheme 2, all the reactions underwent smooth transfer hydrogenative annulation and delivered the desired quinoline products in reasonable to excellent isolated yields (3aa-3ra). Gratifyingly, various functional groups (i.e. -Me, -OMe, -NMe₂, -OH, -Ph, -F, -Cl, -Br, -COOMe and -NO₂) on substrates 1 were well tolerated, and the electrical properties of these functionalities affected the product yields to a certain extent. Especially, reactants 1 bearing electron-withdrawing groups generated the desired product (3ka-3oa) in relatively higher yields that those of substrates containing strong electron-donating substituents (3fa, 3ha) in relatively lower yields that those of substrates containing, presumably because the electron-rich 2-nitrobenzaldehydes are less beneficial to the reduction of the nitro group, whereas the electron-withdrawing groups could enhance the reactivity of the carbonyl group in substrates 1, thus favoring condensation step (Scheme 2). Notably, substrate 10 has two nitro groups, but only one is involved in the formation of product 30a. The unique selectivity is rationalized as the interaction between the carbonyl and ortho nitro groups with the cobalt catalyst.

Subsequently, we turned our attention to the variation of both coupling partners. Thus, the reactions employing various 2-nitroaryl carbonyls and alkynoates **2** were performed under the optimized conditions. As outlined in Scheme 3, all the reactions



Scheme 2. Variation of 2-nitrobenzaldehydes.



Scheme 3. Variation of both coupling agents.

went smoothly and furnished the desired products in moderate to high yields. Both symmetrical and unsymmetrical alkynoates were able to generate the desired product in exclusive regioselectivity (**3lb**, **3fb**, **3ab-3ad**, **3pd**, **3gd**, **3af**). Noteworty, the reaction of 1-(2-nitrophenyl)ethan-1-one **1q** with **2a** did not hamper the product formation (**3qa**), and the somewhat low yield is ascribed to the partial hydrogenation of the C-C triple bond of **2a** due to the relatively low reactivity of substrate **1q**. In addition, the alkynes without an electron-withdrawing group failed to give the quinoline products, indicating that the use of electron-deficient alkynes is essential for the transformation under the current reaction system. In addition to alkynoates, alkynone **2e** is also compatible with the transformation, affording the 3-carbonylquinolines in reasonable yields (**3ae**, **3ee** and **3ne**).

In order to check the stability and reusability of the newly developed catalyst material, we performed the circulation experiments with the model reaction. As presented in Fig. S6 (SI), the reaction conversion has a decreasing trend during the five consecutive runs. After five recycling experiments, the catalyst was detected by ICP-OES, and the cobalt content decreased from 4.21% to 2.95% compared to the fresh catalyst. Therefore, the decreased catalytic activity of the catalyst is attributable to the loss of active cobalt species, which arises out of mechanical wear-induced exfoliation during the course of reaction. In addition, XRD spectra and TEM images of Co/N-ZrO₂@C catalyst after five runs (Fig. S1 and S3a-b in the SI) were examined, the results showed that the morphology of the reused catalyst maintained well.



Scheme 4. Verification experiments.

Next, several verification experiments were performed to gain mechanistic insight into the reaction (Scheme 4). Treating 2nitrobenzaldehyde **1a** under the standard conditions resulted in 2-aminobenzaldehyde **1a'** exclusively, and the retention of the carbonyl group shows that the catalyst exhibits excellent transfer hydrogention selectivity (Eq. (1)). Moreover, the coupling of compound **1a'** with diethyl acetylenedicarboxylate **2a** was able to deliver product **3aa** in 76% yield (Eq. (2)), indicating that compound **1a'** is key a reaction intermediate. These results are in good agreement with the assumed pathway proposed in Scheme 1.

4. Conclusions

In summary, we have developed a new N-doped ZrO₂@C supported cobalt nanocatalyst with uniform dispersion, which exhibits good catalytic performance toward the reductive annulation of 2-nitroaryl carbonyls with alkynoates and alkynones. The catalytic transformation allows synthesizing a wide array of funcitonalized quinolines with the merits of broad substrate scope, good functional compability, excellent transfer hydrogenation selectivity, reusable earth-abundant metal catalyst, and operational simplicity. The developed chemistry paves the ways for further development of hydrogen transfer-mediated coupling reactions by design of heterogeneous catalysts with suitable supports.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2020.01.034.

References

- S.K. Gadakh, S. Dey, A. Sudalai, Rhodium-catalyzed ortho C-H bond activation of arylamines for the synthesis of quinoline carboxylates, Org. Biomol. Chem. 14 (2016) 2969–2977.
- [2] M. Kaur, S. Pramanik, M. Kumar, V. Bhalla, Polythiophene-encapsulated bimetallic Au-Fe₃O₄ nano-hybrid materials: a potential tandem photocatalytic system for nondirected C(sp²)–H activation for the synthesis of quinoline carboxylates, ACS Catal. 7 (2017) 2007–2021.
- [3] W.K. Hu, Y.L. Zhang, H.Y. Zhu, D.D. Ye, D.W. Wang, Unsymmetrical triazolylnaphthyridinyl-pyridine bridged high active copper complexes supported on reduced graphene oxide and their application in water, Green Chem. 21 (2019) 5345–5351.
- [4] Q. Yang, Y.L. Zhang, W. Zeng, Z.C. Duan, X.X. Sang, D.W. Wang, Merrifield resinsupported quinone as an efficient biomimetic catalyst for metal-free, basefree, chemoselective synthesis of 2,4,6-trisubstituted pyridines, Green Chem. 21 (2019) 5683–5690.
- [5] W. Yao, C.Y. Ge, Y.L. Zhang, X.F. Xia, L. Wang, D.W. Wang, Synthesis of 2arylisoindoline derivatives catalyzed by reusable 1,2,4-triazole iridium on mesoporous silica through cascade borrowing hydrogen strategy, Chem. Eur. J. 25 (2019) 16099–16105.
- [6] J. Han, L. Li, Y.Y. Shen, J. Chen, H.M. Deng, M. Shao, X.S. Lu, H. Zhang, W.G. Cao, Copper(1)-catalyzed intermolecular cyclization of methyl perfluoroalk-2ynoates with o-aminophenyl ketones: access to 2-perfluoroalkylated quinolines, Eur. J. Org. Chem. 2013 (2013) 8323–8329.

- [7] B. Duda, S.N. Tverdomed, B.I. Ionin, G.-V. Röschenthaler, Base-promoted heterocyclization of fluorinated alkynylphosphonates with select orthoaminobenzonitriles, Eur. J. Org. Chem. 19 (2012) 3684–3690.
- [8] R. Dayam, L.Q. Al-Mawsawi, Z. Zawahir, M. Witvrouw, Z. Debyser, N. Neamati, Quinolone 3-carboxylic acid pharmacophore: design of second generation HIV-1 integrase inhibitors, J. Med. Chem. 51 (2008) 1136–1144.
- [9] F.W. Bergstrom, Heterocyclic nitrogen compounds. part IIA. hexacyclic compounds: pyridine, quinoline, and isoquinoline, Chem. Rev. 35 (1944) 77– 277.
- [10] S.E. Denmark, S. Venkatraman, On the mechanism of the Skraup-Doebner-Von Miller quinoline synthesis, J. Org. Chem. 71 (2006) 1668–1676.
- [11] M.-E. Theoclitou, L.A. Robinson, Tetrahedron Lett. 43 (2002) 3907-3910.
- [12] O. Nitidandhaprabhas, Doebner's reaction with 6-methyl-2-amino pyridine, Nature 212 (1966) 504–505.
- [13] J.L. Born, Mechanism of formation of benzo[g]quinolones via the Combes reaction, J. Org. Chem. 37 (1972) 3952–3953.
- [14] J. Fan, C. Wan, G. Sun, Z. Wang, Cascade synthesis of 3-quinolinecarboxylic ester via benzylation/ propargylation-cyclization, J. Org. Chem. 73 (2008) 8608–8611.
- [15] B.R. McNaughton, B.L. Miller, A mild and efficient one-step synthesis of quinolines, Org. Lett. 5 (2003) 4257–4259.
- [16] J.M. Muchowski, M.L. Maddox, Concerning the mechanism of the Friedländer quinoline synthesis, Can. J. Chem. 82 (2004) 461–478.
- [17] X.F. Zhang, X.M. Ma, W.Q. Qiu, J. Evansa, W. Zhang, Cascade Knoevenagel and aza-Wittig reactions for the synthesis of substituted quinolines and quinolin-4-ols, Green Chem. 21 (2019) 349–354.
- [18] N.G. Jentsch, J.D. Hume, E.B. Crull, S.M. Beauti, A.H. Pham, J.A. Pigza, J.J. Kessl, M.G. Donahue, Quinolines from the cyclocondensation of isatoic anhydride with ethyl acetoacetate: preparation of ethyl 4-hydroxy-2-methylquinoline-3carboxylate and derivatives, Beilstein J. Org. Chem. 14 (2018) 2529–2536.
- [19] Y.F. Li, Z.G. Wu, J. Shi, Y. Pan, H.Z. Bu, H.F. Ma, J.C. Gu, H. Huang, Y.Z. Wang, L. Wu, FeCl₃-promoted formation of C-C bonds: synthesis of substituted quinolines from imines and electron-deficient alkynes, Tetrahedron. 70 (2014) 8971–8975.
- [20] P. Selig, W. Raven, A convenient allenoate-based synthesis of 2-quinolin-2-yl malonates and β-ketoesters, Org. Lett. 16 (2018) 5192–5195.
- [21] H. Sajjadi-Ghotbabadi, S. Javanshir, F. Rostami-Charati, Nano KF/clinoptilolite: an effective heterogeneous base nanocatalyst for synthesis of substituted quinolines in water, Catal. Lett. 146 (2016) 338–344.
- [22] A. Lenoci, S. Tomassi, M. Conte, R. Benedetti, V. Rodriguez, S. Carradori, D. Secci, S. Castellano, G. Sbardella, P. Filetici, E. Novellino, L. Altucci, D. Rotili, A. Mai, Quinoline-based p300 histone acetyltransferase inhibitors with pro-apoptotic activity in human leukemia U937 cells, Chem. Med. Chem. 9 (2014) 542–548.
- [23] M. Antonello, R. Dante, T. Domenico, O. Prisca, T. Federica, V. Caterina, S. Gianluca, N. Angela, M. Marco, A. Lucia, F. Patrizia, J. Med. Chem. 49 (2006) 6897–6907.
- [24] A.K. Bagdi, S. Santra, M. Rahman, A. Majee, A. Hajra, Synthesis of polysubstituted quinolines via copper(ii)-catalyzed annulation of 2aminoaryl ketones with alkynoates, RSC Adv. 3 (2013) 24034–24037.
- [25] T. Chanda, R.K. Verma, M.S. Singh, InCl₃-driven regioselective synthesis of functionalized/annulated quinolines: scope and limitations, Chem. Asian J. 7 (2012) 778–787.
- [26] R. Xie, F. Xie, C.-J. Zhou, H.-F. Jiang, M. Zhang, Hydrogen transfer-mediated selective dual C-H alkylations of 2-alkylquinolines by doped TiO2-supported nanocobalt oxides, J. Catal. 377 (2019) 449–454.
- [27] X.-W. Chen, H. Zhao, C.-L. Chen, H.-F. Jiang, M. Zhang, Hydrogen-transfermediated alpha-functionalization of 1,8-naphthyridines by a strategy overcoming the over-hydrogenation barrier, Angew. Chem. Int. Ed. 56 (2017) 14232–14236.
- [28] F. Xie, R. Xie, J.-X. Zhang, H.-F. Jiang, L. Du, M. Zhang, Direct reductive quinolyl beta-C-H alkylation by multispherical cavity carbon-supported cobalt oxide nanocatalysts, ACS Catal. 7 (2017) 4780–4785.
- [29] Z. Yuan, B. Liu, P. Zhou, Z. Zhang, Q. Chi, Preparation of nitrogen-doped carbon supported cobalt catalysts and its application in the reductive amination, J. Catal. 370 (2019) 347–356.
- [30] W. Li, J. Artz, C. Broicher, K. Junge, H. Hartmann, A. Besmehn, R. Palkovits, M. Beller, Superior activity and selectivity of heterogenized cobalt catalysts for hydrogenation of nitroarenes, Catal. Sci. Technol. 9 (2019) 157–162.
- [31] W.P. Liu, B. Sahoo, K. Junge, M. Beller, Cobalt complexes as an emerging class of catalysts for homogeneous hydrogenations, Acc. Chem. Res. 51 (2018) 1858– 1869.
- [32] M. Eckardt, M. Zaheer, R. Kempe, Nitrogen-doped mesoporous SiC materials with catalytically active cobalt nanoparticles for the efficient and selective hydrogenation of nitroarenes, Sci. Rep. 8 (2018) 2567.
- [33] K.P. Gong, F. Du, Z.H. Xia, M. Durstock, L.M. Dai, Nitrogen-doped carbon nanotube arrays with high electrocatalytic activity for oxygen reduction, Science 323 (2009) 760–764.
- [34] S. Lu, C. Li, H.H. Li, Y.F. Zhao, Y.Y. Gong, L.Y. Niu, X.J. Liu, T. Wang, The effects of nonmetal dopants on the electronic, optical and chemical performances of monolayer g–C₃N₄ by first-principles study, Appl. Surf. Sci. 392 (2017) 966– 974.

- [35] Y.H. Cao, H. Yu, J. Tan, F. Peng, H.J. Wang, J. Li, W.X. Zheng, N.-B. Wong, Nitrogen-, phosphorous- and boron-doped carbon nanotubes as catalysts for the aerobic oxidation of cyclohexane, Carbon 57 (2013) 433–442.
- [36] J. Wang, Z. Xu, Y. Gong, C.L. Han, H.R. Li, Y. Wang, One-step production of sulfur and nitrogen Co-doped graphitic carbon for oxygen reduction: activation effect of oxidized sulfur and nitrogen, Chem. Cat. Chem. 6 (2014) 1204–1209.
- [37] C.J. Zhou, Z.D. Tan, H.F. Jiang, M. Zhang, Synthesis of (E)-2-alkenylazaarenes via dehydrogenative coupling of (hetero)aryl-fused 2-alkylcyclic amines and aldehydes with a cobalt nanocatalyst, Chem. Cat. Chem. 10 (2018) 2887–2892.
- [38] C.J. Zhou, Z.D. Tan, H.F. Jiang, M. Zhang, A sustainable oxidative esterification of thiols with alcohols by a cobalt nanocatalyst supported on doped carbon, Green Chem. 20 (2018) 1992–1997.
- [39] S.M. Sachau, M. Zaheer, A. Lale, M. Friedrich, C.E. Denner, U.B. Demirci, S. Bernard, G. Motz, R. Kempe, Micro-/Mesoporous platinum-SiCN nanocomposite catalysts (Pt@SiCN): from design to catalytic applications, Chem. Eur. J. 22 (2016) 15508–15512.
- [40] H.L. Jia, B.G. Ren, M. Li, X.J. Liu, J.X. Wu, X. Tan, Structure and electronic properties of Si-doped CeO₂ (111) surface by the first principle method, Solid State Commun. 277 (2018) 45–49.
- [41] R.C. Zhang, X.X. Zhang, M.F. Qian, J.F. Sun, L. Geng, Effect of Si doping on microstructure and martensite transformation in Ni-Mn-Sb ferromagnetic shape memory alloys, Intermetallics 97 (2018) 1–7.
- [42] L. He, F. Weniger, H. Neumann, M. Beller, Synthesis, characterization, and application of metal nanoparticles supported on nitrogen-doped carbon: catalysis beyond electrochemistry, Angew. Chem. Int. Ed. 55 (2016) 12582– 12594.
- [43] F.A. Westerhaus, R.V. Jagadeesh, G. Wienhöfer, M.-M. Pohl, J. Radnik, A.-E. Surkus, J. Rabeah, K. Junge, H. Junge, M. Nielsen, A. Brückner, M. Beller, Heterogenized cobalt oxide catalysts for nitroarene reduction by pyrolysis of molecularly defined complexes, Nature Chemistry. 5 (2013) 537–543.
- [44] J. Yang, F.J. Zhang, X. Wang, D.S. He, G. Wu, Q.H. Yang, X. Hong, Y.E. Wu, Y.D. Li, Porous molybdenum phosphide nano-octahedrons derived from confined phosphorization in UIO-66 for efficient hydrogen evolution, Angew. Chem. Int. Ed. 55 (2016) 12854–12858.
- [45] Q. Zhang, T.R. Zhang, J.P. Ge, Y.D. Yin, Permeable silica shell through surfaceprotected etching, Nano Lett. 8 (2008) 2867–2871.
- [46] W.Q. Wang, L.W. Zh, S. Li, Z.G. Xie, BODIPY-containing nanoscale metalorganic frameworks for photodynamic therapy, Chem. Commun. 52 (2016) 5402–5405.
- [47] Y.L. Cao, S.J. Mao, M.M. Li, Y.Q. Chen, Y. Wang, Metal/Porous carbon composites for heterogeneous catalysis: old catalysts with improved performance promoted by N-doping, ACS Catal. 7 (2017) 8090–8112.
- [48] S.J. Chao, Z.Y. Bai, Q. Cui, H.Y. Yan, K. Wang, L. Yang, Hollowed-out octahedral Co/N-codoped carbon as a highly efficient non-precious metal catalyst for oxygen reduction reaction, Carbon 82 (2015) 77–86.
- [49] L.L. Zhang, A.Q. Wang, W.T. Wang, Y.Q. Huang, X.Y. Liu, S. Miao, J.Y. Liu, T. Zhang, Co-N-C catalyst for C-C coupling reactions: on the catalytic performance and active sites, ACS Catal. 5 (2015) 6563–6572.
- [50] P. Thangasamy, K. Selvakumar, M. Sathish, S.M.S. Kumar, R. Thangamuthu, Anchoring of ultrafine Co₃O₄ nanoparticles on MWCNTs using supercritical fluid processing and its performance evaluation towards electrocatalytic oxygen reduction reaction, Catal. Sci. Technol. 7 (2017) 1227–1234.
- [51] S.C. Cai, Z.H. Meng, H.L. Tang, Y. Wang, P. Tsiakaras, 3D Co-N-doped hollow carbon spheres as excellent bifunctional electrocatalysts for oxygen reduction reaction and oxygen evolution reaction, Appl. Catal. B: Environ. 217 (2017) 477–484.
- [52] X.G. Fu, J.-Y. Choi, P. Zamani, G.P. Jiang, M.A. Hoque, F.M. Hassan, Z.W. Chen, Co-N decorated hierarchically porous graphene aerogel for efficient oxygen reduction reaction in acid, ACS Appl. Mater. Interf. 8 (2016) 6488–6495.
- [53] V. Manivannan, M. Chennabasappa, J. Garrett, Optimization and characterization of lithium ion cathode materials in the system (1-x-y) LiNi_{0.8}Co_{0.2}O₂ • xLi₂MnO₃ • yLiCoO₂, Energies. 3 (2010) 847–865.
- [54] S.M. Chen, J.Y. Cheng, L.T. Ma, S.K. Zhou, X.W. Xu, C.Y. Zhi, W.J. Zhang, L.J. Zhi, J. A. Zapien, Light-weight 3D Co-N-doped hollow carbon spheres as efficient electrocatalysts for rechargeable zinc-air batteries, Nanoscale 10 (2018) 10412–10419.
- [55] X.Y. Li, Q.Q. Jiang, S. Dou, L.B. Deng, J. Huo, S.Y. Wang, ZIF-67-derived Co-NC@CoP-NC nanopolyhedra as an efficient bifunctional oxygen electrocatalyst, J. Mater. Chem. A. 4 (2016) 15836–15840.
- [56] S. Pradhan, S. Roy, S. Ghosh, I. Chatterjee, Regiodivergent aromatic electrophilic substitution using nitrosoarenes in hexafluoroisopropanol: a gateway for diarylamines and *p*-iminoquinones synthesis, Adv. Synth. Catal. 361 (2019) 4294–4301.
- [57] L.N. Wang, S. Li, J.Qu. Shen, Simple and efficient synthesis of tetrahydro-βcarbolines via the Pictet-Spengler reaction in 1,1,1,3,3,3-hexafluoro-2propanol (HFIP), RSC Adv. 4 (2014) 30733–30741.
- [58] I.A. Shuklov, N.V. Dubrovina, Armin Börner, Fluorinated alcohols as solvents, cosolvents and additives in homogeneous catalysis, Synthesis 19 (2007) 2925– 2943.