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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Nitrogen-Coordinated Cobalt Nanocrystals for Oxidative Dehydrogenation and Hydrogenation of N-Heterocycles

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To endow non-noble metals with the high catalytic activity that is typically featured by noble metals is the central yet challenging pursuit for substituting noble metals. In this regard, by exploiting the coordination effect of nitrogen, we prepared cobalt nanocrystals stabilized by nitrogen-doped graphitized carbon (Co NCs/N-C). The obtained Co NCs/N-C catalyst showed extraordinary performances toward both oxidative dehydrogenation of N-heterocycles and its reverse hydrogenation process under extremely mild conditions. A nearly quantitative conversion could be achieved for oxidative dehydrogenation even at room temperature (25 °C), for which the coordination effect of nitrogen is responsible: the interaction of Co-N induces a partial positive charge on the Co surface, thereby promoting the reaction. In contrast, cobalt nanocrystals supported by pristine carbon (Co NCs/C) proved to be inactive for oxidative dehydrogenation, owing to the lack of nitrogen. Moreover, in Co NCs/N-C, the N-doped graphitized carbon formed a protective layer for Co NCs, which preserved the active valence of Co species and prevented the catalyst from leaching. It was found that the catalyst still retained its excellent catalytic activity after five regeneration cycles; in comparison, cobaltous oxide counterpart (CoO_x/N-C) was barely active. As for the mechanism, electron paramagnetic resonance (EPR) analysis revealed the formation of superoxide radical anions during the dehydrogenation process. Interestingly, the pressure of feeding hydrogen showed little effect on the hydrogenation process. Our Co NCs/N-C catalyst is capable of activating molecular oxygen and hydrogen as effectively as noble metals; the coordination effect of nitrogen and the protection of carbon layer in combination confer on the Co NCs/N-C tremendous potential for substituting poble-metal-based catalysts and soluble catalysts for homogeneous reactions.

Introduction

With the rapid progress in the field of catalysis, noble metal catalysts have established dominance in both homogeneous and heterogeneous catalytic systems.¹⁻³ However, the limited reserves and high cost of noble metals severely hinder their large-scale applications and industrialization. To address this issue, extensive attention has been paid to exploiting non-noble metal catalysts⁴ as substitutes, by virtue of their relatively high abundance and low cost. The key concerns on substituting noble metals with non-noble metals are to achieve the superior catalytic activity (generally featured by noble metals) under mild conditions, and in the meantime to keep the non-noble metals intact during the reaction process, since non-noble metals are commonly susceptible to oxidation and leaching, particularly under harsh reaction conditions. To protect the relatively unstable non-noble metals, structural protection by inert layers and the charge balance of non-noble

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metals through interaction with exotic atoms are the two promising strategies. Starting from the first report of metal phthalocyanine complexes tested as cathode catalysts in fuel cells to replace expensive Pt,⁵ numerous transition metal catalysts have emerged in attempts to achieve high catalytic activity like noble metal ones. From the perspective of alternative energy technologies and hydrogen storage, catalytic oxidative dehydrogenation and hydrogenation have received significant attention.⁶ N-heterocycles, a class of pharmacophores broadly present in numerous FDA-approved pharmaceuticals and other bioactive compounds,⁷ are an important research object in this field. In particular, the catalytic oxidative dehydrogenation of saturated N-heterocycles provides one of the most atom-efficient routes⁸ towards yielding high-value products such as indoles, quinolones, and other N-heterocycle aromatic compounds.

To optimize the catalytic system for oxidative dehydrogenation of Nheterocycles and its reverse process, extensive researches have been carried out in homogeneous and heterogeneous catalysis. In the most typical homogeneous catalytic system, Cp*Ir complexes⁹ gave almost quantitative yields for both oxidative dehydrogenation and hydrogenation. Inspired by this work, subsequent reports still focused on noble metals, such as Ir,^{6, 10-11} Ru,¹²⁻¹⁴ Pt,¹⁵ Pd,¹⁵ Rh.¹⁵ In spite of the development of noble metal catalytic systems, great efforts are devoted to exploiting efficient catalysts from sustainable metals so as to circumvent the high cost, high toxicity and low abundance of noble metals. Iron-based^{7, 16} and cobalt-based¹⁷ catalysts are two typical cases, performing at relatively high



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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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temperatures (100 °C or even higher), or under pressurized condition, or for long reaction time. However, some of them still gave barely satisfactory yields. Therefore, up to date it seems that non-noble metal catalysts typically require relatively harsh reaction conditions to deliver acceptable activities. In addition, homogeneous catalysis has an innate limitation in recycling.¹⁸ Whereas for heterogeneous systems, there still exist plenty of challenges to develop inexpensive, earth-abundant metal catalysts instead of the noble metal ones, and meanwhile, to retain superb performances with high activity (under reaction conditions as mild as possible) and robust stability for recycling.

The "heteroatom doping" method resorts to replacing certain carbon lattice atoms with heteroatoms.¹⁹ Nitrogen doping is the most common one, and has proved to be a powerful method to modify carbon materials for various applications.²⁰ Due to the difference in electronegativity between carbon atoms and nitrogen, the nitrogen doping process generally can redistribute the charge density and spin density of carbon atoms in the lattice, thereby effectively regulating the work function and strengthening the adsorption of reactants at specific sites.^{19, 21} In addition, the local geometry in the proximity of dopant nitrogen atoms would be altered due to the difference in atomic sizes between C and the dopant N1, as confirmed by density functional theory (DFT) calculations.²² N-doped carbon nanomaterials are now one of the most important catalytic materials for a wide range of chemical and electrochemical catalytic reactions, such as selective oxidation of aromatic alkanes,²³ reduction of nitrobenzene,²⁴ and hydration of different alkynes,²⁵ oxygen reduction reaction (ORR),²⁶⁻²⁷ hydrogen evolution reaction (HER),²⁸⁻ ²⁹ and overall water splitting.³⁰



Figure 1. The scheme of Co NCs/N-C obtained from the pyrolysis of ZIF-67.

Herein, cobalt nanocrystals stabilized by nitrogen-doped graphitized carbon (Co NCs/N-C) are developed for both oxidative

dehydrogenation of N-heterocycles and its reverse verses of the catalyst exhibits excellent catalytic activity is for 1950 the oxidative dehydrogenation and hydrogenation. Remarkably, even at room temperature without extra O₂ or additional pressure, the Co NCs/N-C can effectively facilitate the oxidative dehydrogenation with a nearly complete conversion. The Co NCs/N-C catalyst is readily recyclable by applying magnetic field and can almost retain its excellent catalytic activity after 5 recycling rounds. It is the first catalytic system for the efficient oxidative dehydrogenation-hydrogenation reaction that proceeds under ambient conditions, which is a fundamental improvement for traditional catalytic methods for organic transformations of N-hetercycles.

Results and discussion



Figure 2. TEM image of ZIF-67 (a) and Co NCs/N-C (b); (c) HAADF-STEM image, corresponding element maps showing the distribution of C (red), N (yellow) and Co (green); d, e, f) TEM image and its magnified images of Co NCs/N-C after acid treatment; g) Magnified HAADF-STEM image of the Co NCs/N-C. h) Atomic resolution STEM image of the Co NC encapsulated in nitrogen-doped carbon; i) Magnified HAADF-STEM image of nitrogen-doped graphitized carbon substrate.

The pyrolysis of metal-organic frameworks (MOFs) at high temperature is an effective and fashionable method for the synthesis of metal/nitrogen-doped carbon composites. Uniform Co-based metal-organic frameworks ZIF-67 nanopolyhedrons can be synthesized from cobalt(II) nitrate (Co(NO₃)₂) and 2-methylimidazole linkers,³¹ and particles with average size of 200-300 nm could be obtained based on reported procedures.³² Then, ZIF-67 was carbonized at high temperature above 700°C for 3 h in a temperature-programmed furnace under a flow of argon. Subsequent treatment with HCl under ultrasonic selectively removed the unprotected cobalt particles generated during the pyrolysis,

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affording the resultant catalyst denoted as Co NCs (Cobalt nanocrystals)/N-C (Nitrogen-doped carbon). The entire synthetic strategy of Co NCs/N-C is shown in Figure S1. The transmission electron microscopy (TEM) images showed that ZIF-67 nanocrystals were all in uniform rhombododecahedral shape (Figure 2a), and the corresponding pyrolysis product well inherited the overall polyhedron-like morphology (Figure 2b), with many Co nanocrystals formed on the carboneous support. Elemental mapping results (Figure 2c) indicated that the Co particles were evenly dispersed in/on the support. Subsequent HCl treatment rendered the support highly porous, with the metallic Co nanocrystals distributed within, as confirmed by the TEM and its magnified images of a single rhombododecahedron (Figure 2d-2f). It is worth mentioning that the Co species are encapsulated in the porous carbon framework (Figure 2g), and the interplanar spacing of Co nanocrystals wrapped in porous carbon is 0.214 nm, corresponding to the Co (111) lattice fringes. Under Aberration-Corrected HRTEM, the surface of encapsulated Co NCs could be clearly observed with atomic-level resolution (Figure 2h). The porous layers having lattice fringes with interplanar distance of 0.340 nm are identified as graphitic carbon (Figure 2i).



Figure 3. a) NEXAFS spectra of Co NCs/N-C b) XANES spectra (the blue area highlights the near-edge absorption energy) and c) Fourier transform (FT) of the ZIF-67, Co NCs/N-C, Catalysts treated in 500 °C H₂, 300 °C Air, and Co-BTC; d) The N K-edge and e) C K-edge of Co NCs/N-C; f) the diagram of Co NCs encapsulated in N-doped carbon.

In the X-ray diffraction (XRD) patterns (Figure S2), the diffraction peaks at 44.2°, 51.5° and 75.8° were respectively ascribed to the (111), (200) and (220) reflections of face-centered cubic cobalt. It is noteworthy that after acid treatment the peak at 26.1° became quite prominent for all three samples (carbonized at 700 °C, 800 °C and

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900°C, respectively), which was indexed to graphitic cathon. This result is also consistent to the HAADF-STEMPIMage1 (Figure 21) 9415% therefore reasonable to infer that acid washing removed not only Co nanocrystals on the surface but also some amorphous carbon, yielding sharper graphitic peaks in the XRD pattern. N-doped graphene is of vital importance for the catalytic performance of the whole material, because the N-doped graphene has been demonstrated to produce defects in graphene support, which result in the formation of active sites for O₂ adsorption.^{16, 33-35} Meanwhile, N-doped graphene also has the ability to reductively adsorb O₂³⁶ and has been employed in the catalytic reduction of nitroarenes³⁷ and for reductive aminations.³⁸

X-ray photoelectron spectroscopy (XPS) further identified the Co valence state of Co NCs/N-C products carbonized at different temperatures (Figure S3); survey spectrum revealed the presence of Co, C, N, and O. The C 1s peak can be deconvolved into two peaks located at 284.1 eV (for typical C-C bond of sp³ carbon) and 284.9 eV (with respect to C-N species), and the one centered at 285.5 eV is the typical graphitic carbon peak. Deconvolution of the N 1s peak indicates that there exist three kinds of nitrogen including pyridinic nitrogen (398.8 eV), pyrrolic nitrogen (400.0 eV), and graphitic nitrogen (401.2 eV) in Co NCs/N-C.³⁹ As for the Co 2p spectrum which can be fitted into two major peaks (Co2p3/2 and Co2p1/2), the peaks around 778.3 eV and 793.3 eV are corresponding to Co⁰, and the two peaks at 780.6 eV and 803.5 eV can be ascribed to Co³⁺, whereas the peaks around 780.1 eV and 796.4 eV are assigned to Co²⁺. It is the two oxidized states not shown in XRD that are the manifestation of the nitrogen-coordination effect. The coordination interaction between nitrogen atom and Co leads to the electron drifting from Co toward nitrogen atom, resulting in slightly positive charge on the metallic surface. Thus, cobalt existing in multiple valences was revealed in XPS data, but only Co⁰ was found in XRD.

We used the synchrotron radiation technique to further investigate the local atomic and electronic structures of Co NCs/N-C. From the NEXAFS spectra resulting from $2p \rightarrow 3d$ dipole transitions, the Co L₃ and L₂ absorption lines are located around 773 eV and 787 eV, respectively. As shown in Figure 3a, the Co L-edge XANES spectra of Co NCs/N-C and Co NCs/C exhibit a peak at the L3-edge, which is characteristic for 3d-electrons, and no well-defined multiple structures are observed; the spectral profiles bear a greater similarity to that of Co rather than Co-based oxides,⁴⁰⁻⁴¹ and the decrease in intensity after nitrogen hybridization implies the higher Co 3d electron occupation in Co NCs/B-C, mainly due to the stronger electronic interactions introduced by nitrogen to the Co NCs.⁴² The X-ray absorption near-edge structure (XANES) curves of Co K-edge (Figure 3b) show that the intensity of the peak A is stronger than that of Co foil and Co NCs/C, indicating the valence state of Co in Co NCs/N-C is slightly higher than that of Co NCs/C and Co foil.⁴³ There is a strong peak located at 2.0 to 2.4 Å, which is related to Co-Co single scattering shown in extended X-ray absorption fine structure (EXAFS) spectra (Figure 3c). From the locally magnified graph (inset in Figure 3c), it was clear that the main peak of Co NCs/N-C is of the

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lowest intensity, suggesting that the Co-Co bond shrinks with the interaction with nitrogen.⁴⁴ In N K-edge spectrum (Figure 3d), the peak at 396.3 eV and the peak at 398.8 eV mainly originated from pyridinic π^* and graphitic π^* transitions, respectively. The peak C at 404.6 eV suggested the formation of C-N-C or C-N σ^* bond. The C Kedge spectrum displayed in Figure 3e shows three peaks: the peak A at 283.9 eV derived from the C-C π^* (ring) excitations, the peak B at 287.0 eV assigned to C-O-C or C-N-C and the peak C at 290.7 eV originating from the C-C σ^* (ring) transitions. The peak A and C suggested that graphitization occurred during the pyrolysis process, while peak B indicated that defect sites existed in the carbon lattice.45 Therefore, the Co NCs/N-C sample obtained after acid treatment show a higher degree of graphitization and more defects in N-C substrate. Based on the above characterizations, it can be inferred that the Co nanocrystals are stabilized by the coordination with nitrogen and the coating with graphitized carbon, as illustrated in Figure 3f. To assess the activity of Co NCs/N-C for the heterocycle oxidative dehydrogenation, we tested the catalyst obtained at 800 °C (denoted as Co NCs/N-C-800 °C) with 1,2,3,4-tetrahydroquinolone as model substrate. Different solvents were screened, and we found that the prepared catalyst in general performed better in polar solvents. When the model reaction was tested at 80 °C in several nonpolar solvents (Table S1) such as p-xylene, 1,4-dioxane, etc., the highest yield obtained was 24.9% after 4 h using p-xylene as solvent. By contrast, polar solvents (Table S2) performed better than all the tested nonpolar solvents. With methanol as solvent, the reaction achieved approximately complete conversion with 100% selectivity at very low temperature (50 °C) after only 4 h (Figure 4b). Even more surprisingly, a conversion of 97.2% could be achieved with longer reaction time (24 h) under room temperature (Table S3).



Figure 4. a) Reaction for oxidative dehydrogenation of 1,2,3,4tetrahydroquinoline; b) Comparisons of conversion and selectivity for different catalysts towards oxidative dehydrogenation; c) Recycling test of the Co NCs/N-C catalyst; d) The DMPO spin-trapping ESR spectra for $\cdot O_2^-$ in this catalytic system.

Next, we compared catalysts carbonized at different pyrolysis temperature with optimized reaction conditions. After 4 h, Co NCs/N-C-700 $^{\circ}$ C and Co NCs/N-C-900 $^{\circ}$ C gave significantly lower

conversions (21.4% and 36.1%, respectively) (Figure 4b) we then assessed the recycling stability of Co NCs/N-C Catalyst 3AS a magnetic catalyst, Co NCs/N-C is of advantage for the ease of separation by applying magnetic field. The Co NCs/N-C could retain its catalytic performance after five-cycle measurements (corresponding morphology shown as Figure S4c, and XRD pattern shown as Figure S5), and no obvious decline in activity was found (Figure 4c). In addition, there was no other by-products observed.

Table 1. N-heterocycle compounds oxidative dehydrogenation with Co NCs/N-C as catalyst.^a

	Substrate	Product	Yield(%) ^b
1			99.9
2	H N H	N N	99.3
3			100.0
4	Br	Br	97.8
5	Meo	MeO	97.5
6	CI	CI	74.3 (93.8) ^c
7	F ₃ C	F ₃ C	99.9
8			96.8
9			17.8
10	MeO NH	MeO N	58.3
11	NH		65.1

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^aReaction conditions: 0.5 mmol substrate, 50 mg catalyst, 3 mL MeOH, air, 50 °C, 12 h; ^bThe yields are determined by GC-MS and GC analysis; ^cReaction conditions: 0.5 mmol substrate, 50 mg catalyst, 3 mL MeOH, air, 50 °C, 24 h; ^dThe molar ratio of Co: substrate in this work is 7.6%.

Under the optimized conditions, we tested the catalyst for other substrates. As shown in Table 1, the catalyst was also efficient for oxidative dehydrogenation of similar substrates under 50 °C in methanol. As expected, substrates with an electron-donating group were active, such as 8-methyl-1,2,3,4-tetrahydroquinoline (entry 1). In addition, 1,2,3,4-tetrahydroquinoxaline (entry 2) and indoline (entry 3) were also quantitatively dehydrogenated under model reaction conditions. Moreover, in spite of the passivation effect of electron-withdrawing group on aromatic rings, substrates with an electron-withdrawing group at the 6 position were well tolerated. 6bromo-1,2,3,4-tetrahydroquinoline (entry 4) and 6-methoxy-1,2,3,4tetrahydroquinoline (entry 5) both gave yields above 97%, while 6chloro-quinoline (entry 6) was produced with a yield of 93.8% under prolonged reaction time. Surprisingly, conditions of 6trifluoromethyl-quinoline (entry 7), the substrate with a strong electron-withdrawing group, was obtain in a yield up to 99.9%. Finally, we test two benzylamines. Remarkably, N-benzylaniline transformed into N-(phenylmethylene)-benzenamine with 96.8% yield (entry 8). Even N-benzylbutan-1-amine obtained in a yield around 20% (entry 9). 1,2,3,4-tetrahydroquinoline substituted with ester, nitro, and 1,2,3,4-tetrahydroisoquinoline gave moderate conversions towards corresponding oxidative dehydrogenation products (entry 10-12).

In light of the afore-mentioned excellent catalytic performance for oxidative dehydrogenation of quinolone, it was imperative to conduct further discussion on the catalytic mechanism. Herein, we investigate the mechanism from the following perspectives: 1) to identify the catalytically active species at the nanoscopic level; 2) to get insights on the chemical environment around the catalytically active species; 3) to explore their active valence states; and finally, 4) to infer the reaction pathway for the oxidative dehydrogenation process.

As shown the TEM images above, there were two kinds of Co NCs in the catalysts, some partially embedded on the surface and some encapsulated in the porous N-doped carbon framework. After treatment with HCl, the Co nanocrystals on surface were removed, and the wrapped ones were acid-resistant and therefore remained intact. The resulting catalyst (denoted as Co NCs/N-C-HCl) was with a cobalt content about 4.5%, as determined by ICP-OES measurement (Inductively Coupled Plasma Optical Emission Spectrometer), in contrast to the untreated catalyst Co NCs/N-C (with 30.4% cobalt content) (Table S4). The activity test of 50 mg Co NCs/N-C-HCl in the model reaction gave a reaction yield as high as 95.5% after 12 h, indicating that Co NCs/N-C-HCl retained almost all the original catalytic activity, even with only one sixth of the family of content. Therefore, it is the Co NCs encapsulated in N-doped carbon framework that essentially drive the reaction during the oxidative dehydrogenation of tetrahydroquinolone, because nitrogen-doped carbon layer prevents the Co nanocrystals from oxidation and deactivation with nitrogen coordination.

To determine the relationship between the N-coordination environment and the catalytic activity, we changed the ligand for MOFs from 2-methylimidazole into 1,3,5-benzenetricarboxylic acid (BTC) (Figure S4d). As a controlled experiment, we modelled on the synthesis method of Co NCs/N-C, and the resulting catalyst was denoted as Co NCs/C-BTC. As confirmed by XPS data (Figure S3), Co NCs/C-BTC contained C, O, and Co, while N could barely be detected. As for the activity test, the Co NCs/C-BTC with 60.0% Co content (measured by ICP-OES) (Table S4) gave a marginal yield of 0.86%. Therefore, the N-coordination environment not only protected the Co NCs from oxidation and deactivation, but also induced electrons to deviate from Co, leading to slightly positive surface charge on the metallic surface, as confirmed by XPS data. This coordination effect further offered an excitation mechanism for the catalytic centers to activate O2, by which the encapsulated Co NCs delivered a remarkable catalytic efficiency.

With the XRD and XPS results, it was determined that Co species in the catalyst was mostly at zero valence state, while local charge existed on the interface between Co NCs and N ligand. For another proof of the catalytic activity of Co⁰, we thermally treated the catalyst (previously carbonized at 800°C) in air at 300 °C and in H₂ at 500 °C, respectively; the products are denoted as Co NCs/N-C-300Air (Figure S4a and S5) and Co NCs/N-C-500H₂ (Figure S4b and S5). After oxidized in air, Co NCs/N-C-300Air only gave a sharply decreased yield of 9.47% after 4 h (Figure S6). Valence state of catalytic species could explain this significant deterioration in performance. After thermal treatment in air, Co NCs were transformed into Co₃O₄, as confirmed by XRD (Figure S5) (so it is also denoted as Co₃O₄/N-C in Figure 4b). The activity of Co³⁺ and Co²⁺ was far below that of Co⁰. As for Co NCs/N-C-500H₂, a yield of 68.3% was achieved (Figure S6). The catalysts gave almost identical XRD patterns (Figure S5) before and after H₂ reduction, and no Co³⁺ peak was found in the Co spectrum. We inferred that H₂ atmosphere at 500°C damaged the coordination interaction between N and Co, which caused the decrease in activity. To verify this inference, Co NCs/N-C-400H₂ was prepared and then tested for comparison. Treated at a lower temperature (400 °C), the catalyst retained most of the catalytic activity with the yield reaching 93.0%, which confirmed the importance of N-coordination for catalytic process.





Figure 5. The mechanism for oxidative dehydrogenation and hydrogenation on three kinds of Co NCs: Co NCs exposed on the nitrogen-doped carbon substrate (left), Co NCs encapsulated with nitrogen-doped carbon (middle), Co NCs encapsulated with carbon (right).

There has been speculation that this reaction progresses via a radical-mediated pathway, which involves the superoxide radical anion $(\cdot O_2^{-})$. Subsequently generated H_2O_2 is quickly consumed, forming quinoline and water.¹⁶ Mechanistic studies on the role of $\cdot O_2^{-}$ in oxidative stress processes are particularly difficult owing to its low steady-state concentration and the lack of highly specific probes that allow its unequivocal identification and guantification.⁴⁶ Herein, we detected $\cdot O_2^-$ by means of electron paramagnetic resonance (EPR). Fortunately, after significantly elevating the concentration of tetrahydroquinoline in the catalytic system, we captured the sextet signal (Figure 4d) that was characteristic for $\cdot O_2^-$. As mentioned above, in N-doped graphene, nitrogen atom doping leads to defects, resulting in the formation of the adsorption active sites for O₂ adsorption and reduction. Therefore, we speculate that the catalytic active species, namely, Co NCs encapsulated by N-doped carbon, could adsorb O_2 from the surrounding air, and donate electrons to reduce O_2 into O_2^- , which drives the oxidative dehydrogenation of tetrahydroquinoline. Under N-coordination environment, the electron "gas" hanging over the surface of Co NCs shifted toward nitrogen atoms, facilitating the electron transfer for $\cdot O_2^-$ production. As a protic solvent, methanol could serve as an outstanding proton donor and transform $\cdot O_2^-$ into HO_2^- , the effective oxidizing species. The stronger the protic solvent, the more significantly the oxidative dehydrogenation was facilitated, which explains the experimental facts that methanol performed best compared with aprotic solvents and other protic solvents tested in this work. Based on the experimental results and our discussion, a plausible reaction mechanism (Figure S7) is proposed.



Figure 6. a) Reaction for hydrogenation of quinoline and conversion vs. temperature b), time c), and pressure d) for hydrogenation;

After achieving efficient catalytic oxidative dehydrogenation of N-heterocycles under relatively low temperatures, we became interested in whether the reverse process, namely, hydrogenation of quinolone to 1,2,3,4-tetrahydroguinoline, could be accomplished using the same catalyst. To evaluate the catalytic activity for hydrogenation, we chose external hydrogen as a hydrogen source, and separately explored the effects of temperature, time, and pressure. We first carried out the hydrogenation reaction in tetrahydrofuran (THF) under 2 MPa pressure for 6 h (Figure 6b), and found that with the increase of temperature, the conversion was obviously elevated. Under ambient temperature (25°C), almost no transformation was detected. However, when the reaction was carried out under 60 °C, the conversion reached 80.0%, and almost quantitative transformation was achieved under 120 °C. Kinetic measurement showed that the reaction rate reached maximum from 0.5 h to 1 h, and conversion kept constant after 6 h (Figure 6c). In addition, the catalytic efficiency is barely affected by the pressure of H₂ (Figure 6d), as confirmed by performance test under different pressures in the range from 1 MPa to 5 MPa. Under 120 °C, hydrogenation of quinoline could be effectively driven in H₂ atmosphere. Based on the above results, it can be concluded that Co NCs/N-C could serve as a bifunctional catalyst for both the oxidative dehydrogenation of N-heterocycles and its reverse process.

Conclusions

In conclusion, we developed a bifunctional catalyst, namely, Co NCs/N-C, which is capable of catalyzing the oxidative dehydrogenation and hydrogenation of N-heterocycles with high efficiencies. Particularly for the oxidative dehydrogenation, the catalyst requires only an extremely mild and simple catalytic system, without extra O₂, relatively high temperature or pressure. Prepared under optimal conditions, the catalyst can promote oxidative dehydrogenation with methanol as solvent at 50 °C in exposure to air, with a nearly complete conversion within 4 h. The activity shows barely any loss after 5-round magnetic regeneration. Through the Co-N coordination effect (nitrogen modulating the electronic structure

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of Co NCs) and the protection effect of carbon layer, we successfully substituted noble metals with inexpensive and readily recyclable transition metal, and significantly elevated the catalytic efficiency. As a result, the oxidative dehydrogenation of N-heterocycles can now be carried out under extremely mild conditions. Compared with conventional catalytic systems, our catalyst offers a highly effective alternative for N-heterocycle transformation, and stands as a new model for converting homogeneous catalytic systems into heterogeneous ones.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Beijing Natural Science Foundation (JQ18007), National Key R&D Program of China (2016YFA0202801, 2017YFA0700101), National Natural Science Foundation of China (21872076, 21573119, 21590792, 21890383), and China Postdoctoral Science Foundation (2018M631444). We thank Institute of High Energy Physics in Beijing and National Synchrotron Radiation Laboratory in Hefei for XAFS measurement.

Notes and references

- Chen, C.; Kang, Y.; Huo, Z.; Zhu, Z.; Huang, W.; Xin, H. L.; Snyder, J. D.; Li, D.; Herron, J. A.; Mavrikakis, M.; Chi, M.; More, K. L.; Li, Y.; Markovic, N. M.; Somorjai, G. A.; Yang, P.; Stamenkovic, V. R., *Science*, 2014, **343** (6177), 1339-1343.
- 2 Chen, Z.; Zhang, Q.; Chen, W.; Dong, J.; Yao, H.; Zhang, X.; Tong, X.; Wang, D.; Peng, Q.; Chen, C.; He, W.; Li, Y., Advanced Materials, 2018, **30** (5), 1704720.
- 3 Wu, Y.; Wang, D.; Zhou, G.; Yu, R.; Chen, C.; Li, Y., Sophisticated Construction of Au Islands on Pt–Ni: An Ideal Trimetallic Nanoframe Catalyst. *Journal of the American Chemical Society*, 2014, **136** (33), 11594-11597.
- 4 Qian, Y.; Du, P.; Wu, P.; Cai, C.; Gervasio, D. F., *The Journal of Physical Chemistry C*, 2016, **120** (18), 9884-9896.
- 5 Jasinski, R., *Nature*, 1964, **201**, 1212.
- 6 Vivancos, Á.; Beller, M.; Albrecht, M., ACS Catalysis 2018, 8 (1), 17-21.
- 7 Chakraborty, S.; Brennessel, W. W.; Jones, W. D., Journal of the American Chemical Society, 2014, **136** (24), 8564-8567.
- 8 Vitaku, E.; Smith, D. T.; Njardarson, J. T., *Journal of Medicinal Chemistry*, 2014, **57** (24), 10257-10274.
- 9 Yamaguchi, R.; Ikeda, C.; Takahashi, Y.; Fujita, K.-i., *Journal of the American Chemical Society*, 2009, **131** (24), 8410-8412.
- 10 Wu, J.; Talwar, D.; Johnston, S.; Yan, M.; Xiao, J., *Angewandte Chemie International Edition*, 2013, **52** (27), 6983-6987.
- 11 Yao, W.; Zhang, Y.; Jia, X.; Huang, Z., Angewandte Chemie International Edition, 2014, **53** (5), 1390-1394.
- 12 Tseng, K.-N. T.; Rizzi, A. M.; Szymczak, N. K., Journal of the American Chemical Society, 2013, **135** (44), 16352-16355.
- 13 He, K. H.; Tan, F. F.; Zhou, C. Z.; Zhou, G. J.; Yang, X. L.; Li, Y., Angewandte Chemie International Edition, 2017, 56 (11), 3080-3084.
- 14 Yamaguchi, K.; Mizuno, N., Angewandte Chemie International Edition, **2003**, 42 (13), 1480-1483.

- 15 Deraedt, C.; Ye, R.; Ralston, W. T.; Toste, F. D.; Someriai, G. A. Journal of the American Chemical Society 2017 control of the 18084-18092.
- 16 Cui, X.; Li, Y.; Bachmann, S.; Scalone, M.; Surkus, A.-E.; Junge, K.; Topf, C.; Beller, M., Journal of the American Chemical Society, 2015, **137** (33), 10652-10658.
- 17 Xu, R.; Chakraborty, S.; Yuan, H.; Jones, W. D., ACS Catalysis, 2015, 5 (11), 6350-6354.
- 18 Du, X.-L.; He, L.; Zhao, S.; Liu, Y.-M.; Cao, Y.; He, H.-Y.; Fan, K.-N., Angewandte Chemie International Edition, 2011, **50** (34), 7815-7819.
- 19 Gao, K.; Wang, B.; Tao, L.; Cunning, B. V.; Zhang, Z.; Wang, S.; Ruoff, R. S.; Qu, L., Advanced Materials **2019**, 31(13), 1805121.
- 20 Gao, Y.; Ma, D.; Hu, G.; Zhai, P.; Bao, X.; Zhu, B.; Zhang, B.; Su, D. S., Angewandte Chemie International Edition 2011, 50 (43), 10236-10240.
- 21 Yan, P.; Liu, J.; Yuan, S.; Liu, Y.; Cen, W.; Chen, Y., *Applied Surface Science* **2018**, 445, 398-403.
- 22 Esrafili, M. D., Computational and Theoretical Chemistry 2013, 1015, 1-7.
- 23 Zhu, Y.; Sun, W.; Chen, W.; Cao, T.; Xiong, Y.; Luo, J.; Dong, J.; Zheng, L.; Zhang, J.; Wang, X.; Chen, C.; Peng, Q.; Wang, D.; Li, Y., Advanced Functional Materials **2018**, 28 (37), 1802167.
- 24 Liu, N.; Ding, L.; Li, H.; Jia, M.; Zhang, W.; An, N.; Yuan, X., Journal of Colloid and Interface Science 2017, 490, 677-684.
- 25 Dreyer, D. R.; Jia, H.-P.; Bielawski, C. W., *Angewandte Chemie* **2010**, 122 (38), 6965-6968.
- 26 Chen, Y.; Ji, S.; Wang, Y.; Dong, J.; Chen, W.; Li, Z.; Shen, R.; Zheng, L.; Zhuang, Z.; Wang, D.; Li, Y., *Angewandte Chemie International Edition* **2017**, 56 (24), 6937-6941.
- 27 Wu, Z.-Y.; Xu, X.-X.; Hu, B.-C.; Liang, H.-W.; Lin, Y.; Chen, L.-F.; Yu, S.-H., Angewandte Chemie International Edition 2015, 54 (28), 8179-8183.
- 28 Chen, W.; Pei, J.; He, C.-T.; Wan, J.; Ren, H.; Zhu, Y.; Wang, Y.; Dong, J.; Tian, S.; Cheong, W.-C.; Lu, S.; Zheng, L.; Zheng, X.; Yan, W.; Zhuang, Z.; Chen, C.; Peng, Q.; Wang, D.; Li, Y., Angewandte Chemie International Edition **2017**, 56 (50), 16086-16090.
- 29 Zhou, W.; Xiong, T.; Shi, C.; Zhou, J.; Zhou, K.; Zhu, N.; Li, L.; Tang, Z.; Chen, S., *Angewandte Chemie International Edition* **2016**, 55 (29), 8416-8420.
- 30 Pan, Y.; Sun, K.; Liu, S.; Cao, X.; Wu, K.; Cheong, W.-C.; Chen, Z.; Wang, Y.; Li, Y.; Liu, Y.; Wang, D.; Peng, Q.; Chen, C.; Li, Y., *Journal of the American Chemical Society* **2018**, 140 (7), 2610-2618.
- 31 Banerjee, R.; Phan, A.; Wang, B.; Knobler, C.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. M., *Science*, 2008, **319** (5865), 939-943.
- 32 Aijaz, A.; Masa, J.; Rösler, C.; Xia, W.; Weide, P.; Botz, A. J. R.; Fischer, R. A.; Schuhmann, W.; Muhler, M., Angewandte Chemie International Edition, 2016, **55** (12), 4087-4091.
- 33 Laurent, S.; Forge, D.; Port, M.; Roch, A.; Robic, C.; Vander Elst, L.; Muller, R. N., *Chemical Reviews*, 2008, **108** (6), 2064-2110.
- 34 Shui, J.-L.; Karan, N. K.; Balasubramanian, M.; Li, S.-Y.; Liu, D.-J., Journal of the American Chemical Society, 2012, **134** (40), 16654-16661.
- 35 Kramm, U. I.; Lefèvre, M.; Larouche, N.; Schmeisser, D.; Dodelet, J.-P., *Journal of the American Chemical Society*, 2014, 136 (3), 978-985.
- 36 Li, J. L., Liu, G. L., Long, X. D., Gao, G., Wu, J., Li, F. W.*, J. Catal., 2017, 355, 53-62.
- 37 Jagadeesh, R. V.; Surkus, A.-E.; Junge, H.; Pohl, M.-M.; Radnik, J.; Rabeah, J.; Huan, H.; Schünemann, V.; Brückner, A.; Beller, M., *Science*, 2013, **342** (6162), 1073-1076.
- 38 Tobias, S.; Annette-Enrika, S.; Marga-Martina, P.; Kathrin, J.; Matthias, B., ChemSusChem, 2014, 7 (11), 3012-3016.
- 39 Yu, Z.; Bai, Y.; Zhang, S.; Liu, Y.; Zhang, N.; Wang, G.; Wei, J.;

Chemical Science Accepted Manuscript

Journal Name

View Article Online DOI: 10.1039/C9SC00475K

Wu, Q.; Sun, K., ACS Applied Materials & Interfaces, 2018, 10 (7). 6245-6252.

- 40 Pengzuo, C.; Tianpei, Z.; Lili, X.; Kun, X.; Yun, T.; Hui, X.; Lidong, Z.; Wensheng, Y.; Wangsheng, C.; Changzheng, W.; Yi, X., Angewandte Chemie International Edition, 2017, 56 (2), 610-614.
- 41 Chang, G. S.; Kurmaev, E. Z.; Boukhvalov, D. W.; Finkelstein, L. D.; Colis, S.; Pedersen, T. M.; Moewes, A.; Dinia, A., Physical Review B, 2007, 75 (19), 195215.
- 42 Chen, L.; Hu, F.; Duan, H.; Liu, Q.; Tan, H.; Yan, W.; Yao, T.; Jiang, Y.; Sun, Z.; Wei, S., Applied Physics Letters, 2016, 108 (25), 252402.
- 43 Yin, P.; Yao, T.; Wu, Y.; Zheng, L.; Lin, Y.; Liu, W.; Ju, H.; Zhu, J.; Hong, X.; Deng, Z.; Zhou, G.; Wei, S.; Li, Y., Angewandte Chemie International Edition, 2016, 55 (36), 10800-10805.
- 44 Junjie, M.; Wenxing, C.; Wenming, S.; Zheng, C.; Jiajing, P.; Dongsheng, H.; Chunlin, L.; Dingsheng, W.; Yadong, L., Angewandte Chemie International Edition, 2017, 56 (39), 11971-11975
- 45 Wenxing, C.; Jiajing, P.; Chun-Ting, H.; Jiawei, W.; Hanlin, R.; Youqi, Z.; Yu, W.; Juncai, D.; Shubo, T.; Weng-Chon, C.; Siqi, L.; Lirong, Z.; Xusheng, Z.; Wensheng, Y.; Zhongbin, Z.; Chen, C.; Qing, P.; Dingsheng, W.; Yadong, L., Angewandte Chemie International Edition, 2017, 56 (50), 16086-16090.
- 46 Hardy, M.; Poulhés, F.; Rizzato, E.; Rockenbauer, A.; Banaszak, K.; Karoui, H.; Lopez, M.; Zielonka, J.; Vasquez-Vivar, J.; Sethumadhavan, S.; Kalyanaraman, B.; Tordo, P.; Ouari, O., Chemical Research in Toxicology, 2014, 27 (7), 1155-1165.

8 | J. Name., 2012, 00, 1-3