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Ordered Porous N-Doping Carbon Matrix with Atomically Dispersed Co Sites as an Efficient Catalyst for Dehydrogenation/Transfer Hydrogenation of N-Heterocycles

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Abstract: The coming single atom catalysts (SACs) as potential substitutes for homogeneous catalysts have been explored widely. Herein, we report an isolated single Co atomic site catalyst stabilized on ordered porous N-doped carbon (ISAS-Co/OPNC). The ISAS-Co/OPNC can be considered as a highly efficient catalyst for acceptorless dehydrogenation of N-heterocycles to release H_2. Importantly, ISAS-Co/OPNC also exhibits excellent catalytic activity for reverse transfer hydrogenation or hydrogenation of N-heterocycles to store H_2 with formic acid or external hydrogen as hydrogen source. The catalytic performances surpass the reported homogeneous and heterogeneous precious metal catalysts. The reaction mechanisms are systematically investigated using first-principles calculations, and the Eley–Rideal mechanism is suggested to be dominating.

Catalytic dehydrogenation and transfer hydrogenation or hydrogenation of N-heterocycles are essential and important processes for organic transformations.[1] Therefore, the dehydrogenation and transfer hydrogenation or hydrogenation of N-heterocycles have received more considerable attention from the opinion of organic hydride hydrogen-storage systems, because the dehydrogenation of N-heterocycles is more feasible compared to that of cycloalkanes through decreasing the endothermicity of the reactions.[2-5] Additionally, acceptorless dehydrogenation of N-heterocycles for releasing H_2 provides a highly efficient process to prepare heterocycles, such as indole, quinoline and their derivatives.[6] Although some homogeneous and heterogeneous metal catalysts have been developed, most of them either can merely perform transfer hydrogenation or hydrogenation, or can just catalyze the opposite dehydrogenation.[7, 8] Nay, those catalysts are mainly homogeneous noble-metal catalysts. Nevertheless, the catalysts, which can perform both dehydrogenation of N-heterocycles and the contrary transfer hydrogenation or hydrogenation of the dehydrogenated N-heterocycles, are very rare.[5, 9]

SACs have attracted the extensive concern of scientific researchers because of their maximum atom utilization, superior reactivity and selectivity.[10] With development of synthetic methodology, plentiful SACs were fabricated successfully. They not only exhibit excellent performance in electrocatalysis, but also show highly catalytic activity for organic transformations, because they can potentially succeed to the merits of homogeneous and heterogeneous analogues.[10] As known to all, the catalytic performances of heterogeneous catalysts are highly dependent upon support materials.[11] The optimal support materials can shorten diffusion pathway and provide sufficient interface area accessible to reactants.[10b, 12] Therefore, extensive applications of SACs still needs to develop rational and general synthetic methods based on support materials.

Quite recently, we developed a template-assistant-pyrolysis (TAP) method for synthesis of SACs.[10b] The reported SACs were studied on electrocatalysis.[10b] Compared with the widely studied electrocatalysis, SACs were seldom explored for organic reactions, let alone catalyzing dehydrogenation and transfer hydrogenation or hydrogenation of N-heterocycles. Herein, we report an ordered porous N-doped carbon catalyst with isolated single Co atomic sites (ISAS-Co/OPNC). With SBA-15 as sacrificial template, ISAS-Co/OPNC was successfully fabricated, and the structure was identified by combining aberration corrected high-angle annular dark-field scanning transmission electron microscope (AC HAADF-STEM) and X-ray absorption fine structure (XAFS) measurements. Interestingly, ISAS-Co/OPNC can perform both dehydrogenation of N-heterocycles to release H_2, and the opposite transfer hydrogenation or hydrogenation of N-heterocycles to store H_2 with formic acid or external hydrogen as hydrogen source. The catalytic activities of ISAS-Co/OPNC for dehydrogenation and transfer hydrogenation or hydrogenation are better than the reported homogeneous and heterogeneous noble-metal catalysts (Table S2 and S4). For comparison, Co-porphyrin and CoNPs/NC were selected as control catalysts and exhibited low activity for dehydrogenation and transfer hydrogenation of N-heterocycles. It is evident that ISAS-Co/OPNC can serve as a fascinating catalyst for dehydrogenation and transfer hydrogenation or hydrogenation of N-heterocycles.

Figure 1a showed the synthetic method of ISAS-Co/OPNC. Low-magnification TEM and field emission SEM images (Figure 1b, 1c and Figure S1) showed ordered porous structure of ISAS-Co/OPNC, which remains the shape of SBA-15. The Co atoms could be identified as the brighter spots on the N-doped carbon from AC HAADF-STEM. Several Co atoms were circled in green

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for better identifications (Figure 1d). The element mappings of ISAS-Co/OPNC suggested C, N and Co were evenly distributed (Figure 1e). The elemental information of nitrogen and cobalt was studied by XPS (Figure S2 and S3). The N 1s spectrum was divided into several peaks at 398.3, 399.1, 400.8, and 404.8 eV assigned to pyridinic N, pyrrolic N, graphitic N, and chemisorbed nitrogen-oxide species, respectively (Figure S2).[13] According to reported studies, the cobalt coordinate with pyridinic N to form catalytically active Co-N_x sites.[10d, 14] XPS revealed that cobalt of Co-porphyrin was in a cationic environment with a high binding energy of Co $2p_{1/2}$ at 780.7 eV (Figure S3). For the pyrolysis of Co-2,2-bipy/SBA-15 (CoCN/SBA-15) and ISAS-Co/OPNC, the Co $2p_{1/2}$ signals down-shifted to 779.1 eV and 780.0 eV. A similar down-shift of Co 2p was observed for CoCN/SBA-15 and ISAS-Co/OPNC, the valence states of the resulting Co were characterized by a slight positive charge because of N-coordination (Figure S3).[15] XRD of ISAS-Co/OPNC demonstrated no cobalt particles (Figure S4). The content of Co was approximately 1.8 wt% determined by ICP-OES analysis. Nitrogen adsorption-desorption isotherms showed that ISAS-Co/OPNC possessed a high BET surface area of 587 m^2 g^{-1} (Figure S5).

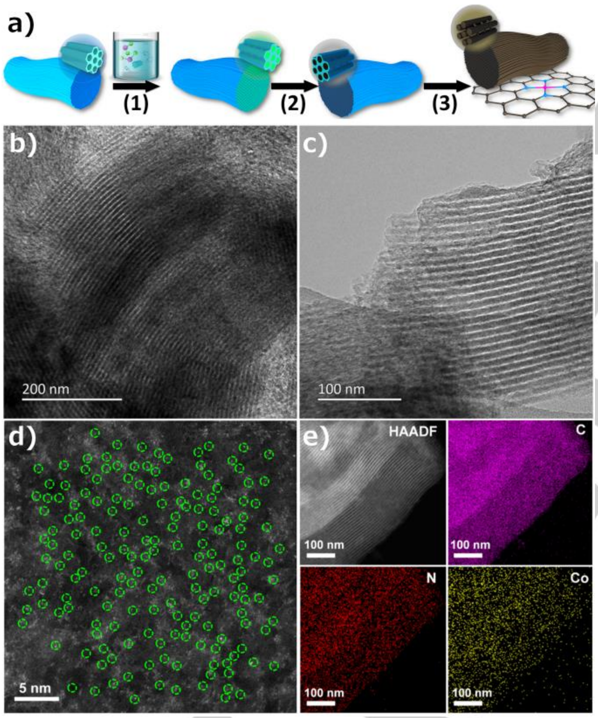

Figure 1. (a) Schematic illustration of the synthesis of ISAS-Co/OPNC. Conditions: (1) 80 °C, H_2O/ethanol, (2) 800 °C, Ar, (3) NaOH. (b, c) TEM images of ISAS-Co/OPNC. (d) AC HAADF-STEM image of ISAS-Co/OPNC. (e) HAADF-STEM image and corresponding EDX mapping of ISAS-Co/OPNC, C (violet), N (red) and Co (yellow).

XAFS measurements were performed to analyze the coordination environment of cobalt at atomic level. Co K-edge X-ray absorption near-edge structure (XANES) spectra of ISAS-Co/OPNC and Co foil, CoO, and Co_3O_4 references were showed in Figure 2a. According to the absorption edge, we conclude that the valence of Co atom situate between Co^0 and Co^{2+}. The valence is not an integer valence, it is an average valence of cobalt. The Fourier transformed (FT) k^3-weighted extended EXAFS spectrum of ISAS-Co/OPNC shows one main peak at 1.44 Å, which belongs to Co−N/C first coordination shell, and no obvious Co−Co peak (2.19 Å) or other high-shell peaks are found (Figure 2b). Therefore, based on AC HAADF-STEM and XAFS results, we believe that cobalt is atomically dispersed. Corresponding EXAFS fitting curves of ISAS-Co/OPNC at *k* and *q* space were shown in Figure 2c and S6. EXAFS fitting was performed to obtain the structural parameters and take out the quantitative chemical configuration of Co atoms (Figure 2d). The coordination number of Co can be confirmed, which is about 4, and the mean bond length is 1.92 Å (Table S1). These data indicate that Co atoms are coordinated by four N atoms in ISAS-Co/OPNC (Figure 2d, inset). In contrast, the best-fit results for Co foil were displayed in Figure S7.

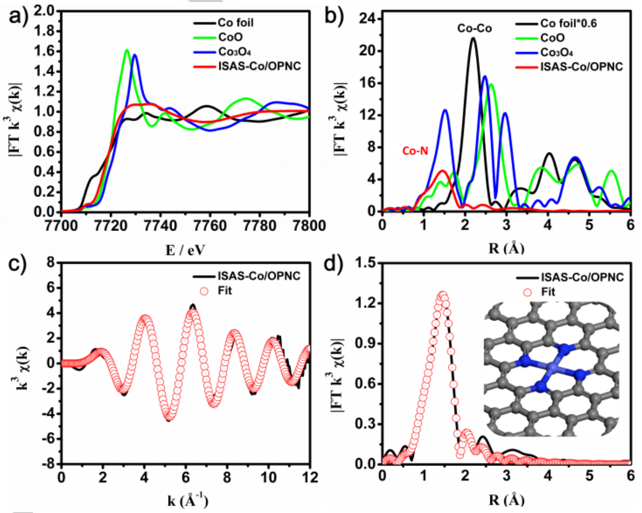

Figure 2. (a) XANES spectra at the Co K-edge of ISAS-Co/OPNC, CoO, Co_3O_4 and Co foil. (b) Fourier transform (FT) at the Co K-edge of ISAS-Co/OPNC and CoO, Co_3O_4 and Co foil references. (c) Corresponding EXAFS fitting curves of ISAS-Co/OPNC at *k* space. (d) Corresponding EXAFS fitting curves of ISAS-Co/OPNC at *R* space. Inset: Schematic model of ISAS-Co/OPNC: Co (light blue), N (dark blue), and C (gray).

To examine the catalytic activity of ISAS-Co/OPNC for dehydrogenation of N-heterocycles, 1,2,3,4-tetrahydroquinoline was chosen as a model substrate. A blank experiment was first tested, but only negligible quinoline was observed (Table 1, entry 1). For contrast, we investigated the catalytic activation of different cobalt materials (Figure S8-S11). As shown in Table 1, besides Co-porphyrin and $CoCl_2$, Co-powder, ZIF-67, CoNPs/NC and CoCN/SBA-15 possessed a lower catalytic activity for the dehydrogenation (Table 1, entries 2-7). However, ISAS-Co/OPNC gave the best performance with 99% conversion of 1,2,3,4-tetrahydroquinoline in air, Ar atmosphere and the presence of butylated hydroxytoluene (BHT) (Table 1, entries 8-10). Indeed, when compared with the reported, it is found that ISAS-Co/OPNC has an excellent activity and milder reaction conditions (Table S2).

We further investigated the dehydrogenation of 1,2,3,4-tetrahydroquinoline derivatives and other N-heterocycles. As

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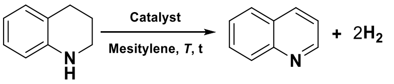
shown in Table S3, 1,2,3,4-tetrahydroquinoline derivatives with an electron-donating group (-Me) was transformed smoothly into the corresponding quinoline compounds with 99% conversion (Table S3, entries 1,2). However, 1,2,3,4-tetrahydroquinoline derivatives with an electron-withdrawing group (-NO_2) was converted slowly into the corresponding quinoline compound with 98% conversion for 18 hours (Table S3, entry 3). 1,2,3,4-Tetrahydroquinoxaline of dual N-heterocycle was catalyzed into quinoxaline with 99% conversion (Table S3, entry 4). Other N-heterocycles like indoline and 6-nitroindoline showed also an efficient conversions and high yields (Table S3, entries 5,6).

Table 1. Cobalt-catalyzed dehydrogenation of N-heterocycles.[a]

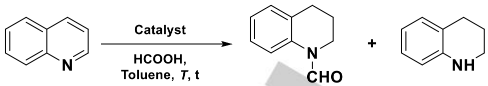


Entry	Catalyst	*T* (°C)	t (h)	Conv. (%)[c]
1	none	120	8	0
2	Co-Porphyrin (6 mg)	120	8	8
3	ZIF-67 (2 mg)	120	8	1
4	$CoCl_2$ (2 mg)	120	8	5
5	Co Powder (2 mg)	120	8	0.5
6	CoNPs/NC (2 mg)	120	8	1.6
7	CoCN/SBA-15 (5 mg)	120	8	2.3
8	ISAS-Co/OPNC (25 mg)	120	8	99
9[b]	ISAS-Co/OPNC (25 mg)	120	8	99
10[b]	ISAS-Co/OPNC (25 mg)	120	8	99

[a] Reaction conditions: The reactions were carried out with 0.5 mmol reactant and Co catalysts (Co = 1.5 mol%) in 1.5 mL of mesitylene. [b] The dehydrogenation of 1,2,3,4-tetrahydroquinoline performed in Ar atmosphere and the presence of BHT. [c] Determined by GC analysis using of *n*-dodecane as internal standard.

We further explored transfer hydrogenation of quinoline to 3,4-dihydroquinoline-1(2*H*)-carbaldehyde (2a) with formic acid as the hydrogen source. Transfer hydrogenation of quinolines were tested under almost the same conditions as that of the above dehydrogenation reaction. The product 2a can be easily hydrolyzed into the corresponding amine, 1,2,3,4-tetrahydroquinoline (2b), in quantitative yield simply by using NaOH/H_2O/EtOH (Scheme S1).[7d] As expected, ISAS-Co/OPNC possessed the best catalytic activity with 99% quinoline conversion and 99% 3,4-dihydroquinoline-1(2*H*)-carbaldehyde selectivity (Table 2, entry 8). However, for blank experiment and different cobalt materials, their catalytic performances of transfer hydrogenation can be trifling (Table 2, entries 1-7). When the reaction was carried out at 100 °C, the reaction time just prolonged to 4 hours (Table 2, entry 9). In order to verify the activation of external hydrogen for quinoline hydrogenation, the experiment of external hydrogen as a hydrogen source was performed. It was found that quinoline was converted completely into 1,2,3,4-tetrahydroquinoline under 120 °C, 1.5 MPa and 50 mg (3 mol% Co) catalyst in 1.5 mL toluene for 12 hours. In like wise, compared with the reported results, whether using formic acid or external hydrogen as a hydrogen source, ISAS-Co/OPNC has also an outstanding catalytic activity (Table S4).

Table 2. Cobalt-catalyzed transfer hydrogenation of quinoline with formic acid.[a]



2a

2b

Entry	Catalyst	Conv. (%)[c]	Sel. (%)[d]	
			2a	2b
1	none	trace	trace	trace
2	Co-Porphyrin (6 mg)	3	91	9
3	ZIF-67 (2 mg)	1.1	97	3
4	$CoCl_2$ (2 mg)	0.8	99	trace
5	Co Powder (2 mg)	0.2	93	7
6	CoNPs/NC (2 mg)	6	99	trace
7	CoCN/SBA-15 (5 mg)	1.2	99	trace
8	ISAS-Co/OPNC (25 mg)	99	99	trace
9[b]	ISAS-Co/OPNC (25 mg)	99	99	trace

[a] Reaction conditions: The reactions were carried out with 0.5 mmol reactant, 1.5 mol % Co catalyst and 10 eq. HCOOH in 1.5 mL of toluene at 120 °C for 1.5 hours. [b] The reaction was performed at 100 °C for 4 hours. [c] Determined by GC analysis with n-dodecane as internal standard. [d] Determined by GC-MS analysis.

ISAS-Co/OPNC was also conducted for transfer hydrogenation of a broad scope of N-heterocycle substrates. The reaction results were listed in Table S5. We can observe that quinoline-derivatives with electron-donating group (-Me or -OMe) were completely converted to corresponding 3,4-dihydroquinoline-1(2*H*)-carbaldehyde derivatives (Table S5, entries 1-5). 6-Methoxyquinoline was nine tenths converted into 6-methoxy-3,4-dihydroquinoline-1(2*H*)-carbaldehyde (Table S5, entry 6). Moreover, for quinoline derivatives with electron-withdrawing group (-Cl or -Br), transfer hydrogenation conversion were also more than 90% (Table S5, entries 7-9). Apart from the routine substituted quinoline derivatives, other N-heteroarenes such as 7,8-benzoquinoline remained suitable reactant for this reaction converting into the corresponding formamide in moderate to excellent conversion with high selectivity (Table S5, entry 10). Moreover, the hydrogenation of quinoline derivatives with external hydrogen as hydrogen source were also performed under (Table S6). Quinoline derivatives with a methyl was transformed into the 1,2,3,4-tetrahydroquinolines compounds with 99% conversion (Table S6, entries 2,3). However, 2,6-dimethyl-quinoline was converted slowly into the corresponding tetrahydroquinoline with 95% conversion (Table S6, entry 4). For quinoline derivatives with electron-withdrawing group (-Cl or –NO_2), the hydrogenation conversion were also high impressive (Table S6, entries 5,6).

For heterogeneous catalysis, to avoid the deactivation of the catalysts resulted from aggregation and leaching of active metal during the reaction is still a challenging. Therefore, the reusabilities of ISAS-Co/OPNC in dehydrogenation and transfer hydrogenation were investigated. For this purpose, ISAS-Co/OPNC was separated from the reaction system by centrifugation, washed and dried at 100 °C under vacuum, and then reused. It was worth mentioning that no obvious attenuation of catalytic activation was observed. After six runs, the conversions of the target products were still up to 99% for both dehydrogenation and transfer hydrogenation (Figure S12). In addition, when ISAS-Co/OPNC was filtered off, the further reaction could not be observed (Figure S13 and S14). Figure S15 and S16 showed that cobalt was still homogeneously distributed and exhibited a little differences on the morphology after six runs. Thereby, it demonstrated that the aggregation and leaching of active centers did not occurred during dehydrogenation and transfer hydrogenation.

Since the basic reactions of hydrogenation and dehydrogenation of quinoline are similar, the hydrogenation reaction was taken as an example to study the mechanism. To understand the reaction mechanism and energetics, we carried out first-principles calculations of 1,2,3,4-tetrahydroquinoline hydrogenation. Hydrogen was chosen as the reductant to simply the calculations, and the dissociation of hydrogen was assumed to be in equilibrium. All the possible pathways were considered, and the free energy profile of the most favorable pathway are shown in Figure S17. It can be seen that the reaction starts with the hydrogenation of N atom in 1,2,3,4-tetrahydroquinoline forming IM1. Then, the carbon next to nitrogen couples with H forming partially hydrogenated product (p-product). The rest two carbon are hydrogenated via intermediate state, IM2, giving the final product. The hydrogenation of p-product is favorable both thermodynamically and kinetically, suggesting the p-product is likely to be hydrogenated on ISAS-Co/OPNC. This finding is in agreement with the experiment result that no p-product is detected. Furthermore, all the barriers of the four hydrogen elementary steps are lower than 0.87 eV, indicating the single Co site are highly active for the hydrogenation of 1,2,3,4-tetrahydroquinoline. Interestingly, all the most favorable transition states are *via* Eley–Rideal (ER) mechanism, in which hydrogen is on the Co site and the quinoline species attracts from gas-phase (Figure S18b). The transition states geometries of the elementary steps with highest barriers, namely the last hydrogenation step, via Langmuir–Hinshelwood (LH) and ER mechanism are shown in Figure S18. The barriers of LH and ER are calculated to be 1.73 eV and 0.87 eV, indicating ER mechanism is likely to be dominating in the 1,2,3,4-tetrahydroquinoline hydrogenation on the ISAS-Co/OPNC.

In conclusion, we successfully prepared an atomically dispersed ISAS-Co/OPNC catalyst, which exhibited highly efficient catalytic activities for both dehydrogenation of N-heterocycles to release H_2 and the reverse transfer hydrogenation or hydrogenation of N-heterocycles to store H_2 with formic acid or external hydrogen as hydrogen source. The catalytic activities for dehydrogenation and transfer hydrogenation or hydrogenation of N-heterocycles exceeded the reported homogeneous or heterogeneous noble-metal catalysts due to the lower barriers *via* ER mechanism. Organic materials that are amenable to catalyzed reversible dehydrogenation/hydrogenation may be used as hydrogen-storage materials, with potential to generate H_2 and thereby substitute petroleum fuel.

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Keywords: ordered porous • N-doping carbon matrix • atomically dispersed sites • dehydrogenation • transfer hydrogenation or hydrogenation

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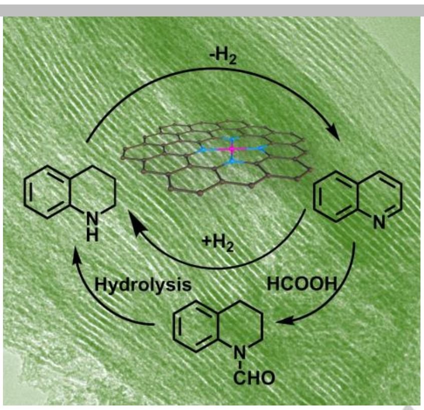
Isolated single Co atomic site catalyst stabilized on the ordered porous N-doped carbon matrix (ISAS-Co/OPNC) shows highly efficient catalytic performance for both the acceptorless dehydrogenation of N-heterocycles to release H_2 in mesitylene at 120 °C for 8 hours, and the reverse transfer hydrogenation or hydrogenation reaction of N-heterocycles to store H_2 in toluene at 120 °C with formic acid or external hydrogen as hydrogen source.



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Ordered Porous N-Doping Carbon Matrix with Atomically Dispersed Co Sites as an Efficient Catalyst for Dehydrogenation/Transfer Hydrogenation of N-Heterocycles