Recent Insight in Transition Metal Anchored on Nitrogen-Doped Carbon Catalysts: Preparation and Catalysis Application

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Abstract: The design and preparation of novel, high-efficiency, and low-cost heterogeneous catalysts are important topics in academic and industry research. In the past, inorganic materials, metal oxide, and carbon materials were used as supports for the development of heterogeneous catalysts due to their excellent properties, such as high specific surface areas and tunable porous structures. However, the properties of traditional pristine carbon materials cannot keep up with the sustained growth and requirements of industry and scientific research, since the introduction of nitrogen atoms into carbon materials may significantly enhance a variety of their physicochemical characteristics, which gradually become appropriate support for synthesizing supported transition metal catalysts. In the past several decades, the transition metal anchored on nitrogen-doped carbon catalysts has attracted a tremendous amount of interest as potentially useful catalysts for diverse chemical reactions. Compared with original carbon support, the doping of nitrogen atoms can significantly regulate the physicochemical properties of carbon materials and allow active metal species uniformly dispersed on the support. The various N species in support also play a critical role in accelerating the catalytic performance in some reactions. Besides, the interaction between support and transition metal active sites can offer an anchor site to stabilize metal species during the preparation process and then improve reaction performance, atomic utilization, and stability. In this review, we highlight the recent advances and the remaining challenges in the preparation and application of transition metal anchored on nitrogen-doped carbon catalysts.

Keywords: nitrogen-doped porous carbon support; metal catalyst; heterogeneous catalysis; organic reactions

1. Introduction

The processes of chemical synthesis and transformation rely heavily on the use of catalysts. The catalysts can significantly reduce the activation energy of the reaction and further control the conversion and selectivity. In modern chemical industries, catalysts play an important role in the synthesis of high-value-added fine chemicals, pharmaceuticals, agrochemicals, dyes, food additives, resins, and other products [1,2]. According to the statistics, approximately 90% of the chemicals are obtained through catalytic processes [3,4]. Therefore, catalysts are becoming the most essential driving factors behind both the fast expansion of industry production and the progression of scientific research. Designing and developing catalysts with high catalytic efficiency greatly enhance reaction activity and product selectivity in chemical processing, further improving production efficiency and economic development. Additionally, the demand for sustainable and clean energy in modern society is growing enormously. The catalysis transformation has been recognized as one of the most important fields with crucial solutions to this growing issue. The catalysts not only eliminate a lot of energy employed in chemical industry processes but...
also take part in the majority of the energy transformation reactions, such as hydrogen production, synthesis of fuel cells, and reduction of CO₂ emissions [5–7]. In addition, utilizing the appropriate catalysts could result in milder and more ecologically friendly reaction conditions [8]. Therefore, the construction of high activity, stable, and cost-effective catalysts is essential for green chemistry and sustainable development.

In recent years, heteroatom-doped carbon materials have been extensively investigated and used in the fields of catalysis, functional material, energy storage, etc. [9,10]. Doping carbon materials with heteroatoms has dramatically improved their physicochemical properties, allowing them to be used in a broader range of applications. Among the various heteroatoms, nitrogen is the most widely research and applies in heteroatoms-doped carbon materials. Since the nitrogen atoms have similar atomic radii and more valence electrons than carbon atoms, making it is easier to bond with the carbon matrix while maintaining the original structure of the carbon material [11]. The doping of N atoms can significantly regulate the physicochemical properties of the material, such as thermal stability, acidity, alkalinity, wettability, and electronic structure [12]. In addition, the doping of nitrogen atoms can form a certain number of defective sites in the carbon structure and increase the electron mobility in the material through the conjugation effect. Furthermore, nitrogen atoms may significantly increase the dispersion and stability of the transition metal species on the carbon support and strengthen the synergistic effect between the support and metal active site, further enhancing the catalytic performance of the catalyst [13,14]. Transition metals feature unoccupied valence d orbitals that can take and provide electron pairs. Since they can speed up reactions that require electron transfer, they are often used as active sites for supported catalysts [15]. In addition, they can assist in stabilizing critical intermediate chemicals in reactions, therefore enhancing the efficiency of the reactions [16]. Transition metal active sites are presented as nanoparticles, clusters, and single atoms, all of which have elevated surface energies and are especially prone to aggregation and leaching during catalyst preparation and catalytic reactions [17]. Furthermore, the stability and dispersion of metal species may be considerably enhanced by using metal-support interactions to prevent their aggregation and leaching. The interaction between metals and support may also cause charge transfer between metals and reactants, which dramatically boosts the activity of active sites and thus accelerates the reaction rate [18].

The doping of nitrogen atoms improves the physicochemical properties of carbon materials with high specific surface area, abundant porous structure, nitrogen-containing groups, and defect sites, which are the ideal support for the preparation of transition metal heterogeneous catalysts [19,20]. On this basis, further introduction of transition metals as active sites into nitrogen-doped carbon support can significantly improve the catalytic performance and realize more comprehensive applications. It is shown that metals can be coordinated with nitrogen atoms to form M-Nₓ (M = Fe, Co, Ni, Cu, Zn, etc.) groups and regulate the electronic structure of the catalyst by changing the local coordination environment, thus optimizing the charge transfer redistribution and adsorption energy on the substrate and intermediate adsorbed on the metal surface and ultimately improving the reaction performance [21]. Nitrogen doping can also change the surface physical and chemical properties of carbon materials by modulating the electronic structure, thus enhancing the metal-support interaction. Metal-support interactions affect the adsorption, nucleation, growth, and deposition of metal species during preparation, resulting in changes in the dispersion and crystallinity of the metal species, which are crucial for catalytic performance [1,22]. Therefore, it is of great practical importance to research and develop a heterogeneous catalyst with high catalytic performance and stability by employing N-doped porous carbon materials as support and transition metals as active sites.

In this review article, we try to briefly discuss the latest developments of transition metal anchored on nitrogen-doped carbon catalysts, covering the methodologies for the catalysts synthesis as well as their catalytic application in a variety of different organic processes (hydrogenation, oxidation, dehydrogenation, and hydroformylation) and electro-catalysis reactions.
2. Preparation Method of Transition Metal Anchored on Nitrogen-Doped Porous Carbon Catalysts

Research on the synthesis of transition metals anchored on nitrogen-doped porous carbon catalysts has advanced rapidly in the past few years. The homogeneous dispersion of metals on a suitable support is one of the critical methods to improve the catalytic performance since higher dispersion usually represents higher active site utilization, which can further enhance the catalytic activity of the catalyst. On the other hand, the performance of the catalyst is closely related to the choice of metal precursors, support, and synthesis methods. Therefore, it is crucial to select a suitable synthesis method to prepare nitrogen-doped carbon-supported transition metal catalysts based on the properties of the metal precursors and nitrogen-doped carbon support. There are various methods for synthesizing this kind of catalyst, such as the post-loading method, simultaneous introduction of metals and nitrogen into pre-synthesized carbon support, in situ pyrolysis method, etc. [8]. Table 1 provides a concise summary of the pros and cons of these different methods. This part briefly discusses typical synthesis methods used for transition metal anchored on N-doped carbon catalyst.

Table 1. The advantage and disadvantage of different synthesized methods of transition metal anchored on N-doped carbon catalyst.

| Entry | Preparation Methods | Advantage | Disadvantage |
|-------|---------------------|-----------|--------------|
| 1     | Post-loading        | Controllable structure and morphology, Uniform particle size, High utilization of active sites | Complex synthesis processes, Lower metal loading rate |
| 2     | Simultaneous introduction of metals and nitrogen into pre-synthesized carbon support | Adjustable nitrogen content, High-dispersed metal sites | Uncontrollable active size |
| 3     | In-situ pyrolysis   | Adjustable nitrogen content, High-dispersed metal sites, Simplest synthesis steps and time-saving operation | Uncontrollable active size, Active sites are easily confined by N-doped carbon framework, Precious metals easily aggregate |

2.1. Post-Loading Method

In the past decades, the post-loading method has prepared most of the transition metals anchored on N-doped carbon catalysts [3,23,24]. The N-doped carbon materials were first obtained by post-treatment or direct synthesis from N-containing precursors, and then the metal species were supported onto the N-doped carbon support by impregnation adsorption of metal cations via the post-loading method. Then the metal species anchored on the surface of the N-doped carbon were further reduced to finally form metal anchored on N-doped carbon catalysts. The post-loading method can utilize different physicochemical conditions and template effects to synthesize the desired morphological structure, and different catalyst preparation methods can be chosen according to the nature of the N-doped carbon material. Since the structure and size of the catalyst support have been chosen by this process, catalysts with the desired specific surface area, pore size, and other parameters could well be synthesized. In addition, the catalysts synthesized by this method usually have a high utilization rate for metal active sites [23]. However, the biggest issue with this method is the relatively tedious preparation process and how to enhance the loading rate of metal species. Generally, the synthesis of transition metal anchored on N-doped carbon catalysts includes three steps: the preparation of nitrogen-doped carbon support, the adsorption-deposition of metal precursors, and finally the reduction of metal precursors to the metallic state. The conventional post-loading methods mainly include impregnation and deposition-precipitation methods.
2.1.1. Impregnation Method

Impregnation is an efficient and straightforward method for the synthesis of heterogeneous catalysts and is widely utilized in industrial catalyst preparation [24]. The process starts with dissolving the metal precursor (usually a salt) in a suitable solvent, then adding N-doped carbon support to the solution with sufficient stirring and adsorption, and finally removing the solvent and drying, calcining, or reducing the synthesized solid to obtain the final catalyst. Among the various post-loading methods, the impregnation method is one of the most commonly used methods in the synthesis of heterogeneous catalysts due to its simple procedure. Almost all carbon materials and soluble metal salts can be used as supports and metal precursors, respectively. The method can be used to control the metal loading by varying the concentration of the metal precursor solution. Huang and co-workers created N-doped carbon-supported Co nanoparticle catalysts through the impregnation method [25] (Figure 1). First, a certain amount of Co(OAc)$_2$·$4$H$_2$O and [MC-NIm]Cl were mixed and dissolved in methanol and stirred for 30 min. Then the activated carbon powder was added, and the mixture was stirred at 50 °C for five hours. Finally, the methanol has been removed, and the obtained solid precursor is next pyrolyzed at 800 °C for two hours in a nitrogen atmosphere to synthesize Co@NC (800-2 h) catalysts. However, due to the different diffusion resistance between the outer and inner surfaces of the N-doped carbon support, some metal precursors may be adsorbed on the outer surface of the support, resulting in aggregation into larger particles on the surface [26].

![Figure 1](image_url). The procedure for the synthesis of Co@NC (800-2 h). Reprinted with permission from Ref. [25]. Copyright © The Royal Society of Chemistry 2018.

2.1.2. Deposition-Precipitation Method

In order to obtain complete precipitation of the metal compounds, this method involves the dissolving of metal precursors, which is then followed by an adjustment to the pH, temperature, or evaporation of the solvent [27]. After the precipitation–deposition step, the catalyst is filtered, washed, dried, and reduced after being deposited on the surface of the nitrogen-doped carbon material. Firstly, these metal compounds are deposited on the surface of the material. The generation of tiny metal hydroxides in the liquid phase is the most essential stage of the synthesis process. The impregnation method is often used to generate catalysts with metal loadings that are lower than those prepared using the deposition-precipitation method, which is typically restricted by solubility [28]. With these properties, this approach is particularly effective for the preparation of low metal loading catalysts. Most significantly, all of the active components are preserved on the surface of the support, so it is possible to create a particle size distribution that is uniform across the board. The preparation procedure, on the other hand, must ensure that the local concentration of the solution does not exceed the critical supersaturation level. Besides, the nucleation process may occur in the solution rather than on the support. This is necessary to ensure that the nucleation process of the metal species is not entirely under the control of the researcher. Moreover, the metal particles generated by this method are often large and less uniform.
2.2. Simultaneous Introduction of Metals and Nitrogen into Pre-Synthesized Carbon Support

The conventional post-loading method is the most classical and efficient way to synthesize transition metal anchored on N-doped carbon catalysts, but the preparation process is often time-consuming. Researchers have created and developed a novel method by introducing both metal and nitrogen atoms on a pre-synthesized carbon support in order to more effectively manufacture the target catalysts. Then the transition metal anchored on N-doped carbon catalysts can be obtained by pyrolysis of the mixtures of metal salts, nitrogen-containing precursors, and carbon support. For instance, Beller et al. prepared a metal nanoparticle catalyst loaded on nitrogen-doped carbon by high-temperature pyrolysis of mixtures of non-volatile organometallic amine complexes and carbon support, in which the metal complexes were completely decomposed during carbonization to establish active metal nanoparticles and nitrogen-doped carbon [29]. Furthermore, the simultaneous introduction of metal and nitrogen species can reduce many of the steps required to modify carbon support with nitrogen atoms and metal species. The N content of catalysts can be effectively controlled by varying the amount of nitrogen-containing precursor used in this method, which could further regulate the physical and chemical properties of the support as well as the electronic structure and synergistic effects between N-doped carbon support and metal species.

2.3. In-Situ Pyrolysis Method of Transition Metal Anchored on Nitrogen-Doped Carbon Catalysts

Although the aforementioned approaches have successfully designed and prepared transition metal anchored on N-doped carbon catalysts, there is still an urgent need for a simple and efficient one-step synthesis method. In view of this, researchers have developed one of the simplest and most straightforward synthesis approaches by mixing metal precursors, nitrogen precursors, and carbon precursors together and then obtaining transition metal anchored on N-doped carbon catalysts by a one-step pyrolysis method.

Recently, Kang et al. developed a novel atomic Fe and N co-doped carbon catalyst (meso-Fe-N-C) by in situ pyrolyzing a mixture of dopamine, F127, and ammonium ferrous sulfate (Figure 2) [10]. The dopamine was employed as a C and N source which can easily be transformed to quinone and then self-polymerized into polydopamine (PDA), and F127 was used as a soft template for the establishment of mesostructure. During the reaction, Fe-coordinated dopamine was self-polymerized to Fe/PDA/F127 composites with mesoporous structures, which were then pyrolyzed to produce the N-doped carbon nanosheet supported single Fe atom catalysts. It is worth noting that N-doped carbon prevented Fe atoms from aggregating and facilitated the formation of active Fe-N-C sites. This preparation approach is step and time-efficient. In addition, the structure and nitrogen content of the catalysts may be modified by adjusting the synthesis conditions and the addition of N-containing compounds. Nevertheless, the approach has certain drawbacks. For instance, supported metal catalysts prepared by high-temperature in situ pyrolysis (especially for non-precious metals) consist of nanoparticles with an extensive particle size distribution, where not only exposed or encapsulated metal nanoparticles can be observed but also highly dispersed single atoms that are not visible under electron microscopy. All of these factors make it challenging to identify the true active site in this research. In addition, this method is unsuitable for producing nitrogen-doped carbon-supported noble metal catalysts since most noble metals have a significant tendency to aggregate at high temperatures. Furthermore, some of the metal nanoparticles may be entirely trapped in the nitrogen-doped carbon matrix, thus reducing the accessibility of the catalytic activity to the reactants.
3. Catalytic Application

Because the doping of nitrogen atoms have the ability to modify the characteristics of carbon material and combined with the synergistic effect of nitrogen atoms and transition metal active sites, it has the great potential to enhance the catalytic performance as well as the stability of the catalysts. In addition, the nitrogen dopants may efficiently change the electronic structure of carbon support. This finding dramatically improves the catalytic efficiency of the carbon support by facilitating the adsorption and desorption of intermediates throughout the reaction process. The stability of metal species in catalytic processes may be further improved by using nitrogen-doped porous carbon support, which can make the metal uniformly dispersed and efficiently prevent aggregation and leaching. Therefore, transition metals anchored on nitrogen-doped carbon have a broad variety of applications in the fields of traditional heterogeneous catalysis, energy storage materials, and photocatalysis [9,30,31]. Here, we summarized various thermocatalytic organic reactions catalyzed by these kinds of catalysts in this section.

3.1. Hydrogenation Reactions

Catalytic hydrogenations are used in the synthesis of various central intermediates and high-value-added chemicals. Depending on the hydrogen source, hydrogenation reactions can be classified into two categories: direct hydrogenation and transfer hydrogenation. The direct hydrogenation typically utilizes molecular hydrogen as the hydrogen source, whereas transfer hydrogenation utilizes hydrogen storage compounds such as alcohols and acids as the hydrogen source. In recent years, transition metals anchored on nitrogen-doped carbon catalysts with good catalytic activity and stability have been recognized as promising nanocatalysts in both types of selective hydrogenation reactions. Thomas et al. prepared cobalt nanoparticles on a mesoporous nitrogen-doped carbon supports catalyst (CN1meso-Co) which exhibited excellent conversion and selectivity in the hydrogenation reaction of nitroaromatics under mild conditions [30]. The scheme of the catalysts and reaction is depicted in Figure 3. The high surface area, porous structure, and the abundant N atoms on the support were proved to be extremely vital for dispersing and stabilizing the active Co species. In comparison to catalysts using silica, alumina, or mesoporous carbon as support, cobalt species supported on nitrogen-doped carbon material allowed for more uniform dispersion and stability of the metal species, which could make the obtained catalysts better performance in the catalytic reactions. In addition, the theoretical calculation suggested the N-species could serve as a site for H$_2$ adsorption and subsequent
heterolytic cleavage with the assistance of Co nanoparticles. Thus, the remarkable catalytic activity of the CN1meso-Co catalyst may be attributed to the aforementioned factors.

Figure 3. A nitrogen-doped carbon supported cobalt nanoparticle catalyst (CN1meso-Co) for nitrobenzene hydrogenation. Reprinted with permission from Ref. [30]. Copyright © American Chemical Society 2020.

In 2022, Dong and colleagues reported ultrafine Ru nanoparticles anchored on the hierarchal porous N-doped carbon nanospheres (HPNC) catalysts (Figure 4) [31]. The N-doped carbon nanospheres with a high specific surface area and a hierarchically porous structure were created using a simple and versatile nano-emulsion and self-assembly strategy, and the Ru nanoparticles were uniformly dispersed and reduced on the obtained N-doped carbon material. The unique structure of HPNC support significantly prevented ultrafine Ru nanoparticles from aggregating and leaching, resulting in uniform distribution over the support and more accessible active sites for reactant adsorption. The synthesized Ru/HPNC catalysts exhibited excellent catalytic performance for biomass-derived levulinic acid (LA) hydrogenation to γ-valerolactone (GVL) under solvent-free conditions with outstanding catalytic activity and reusability. In order to gain a better understanding of the roles that the support played and their effect on the performance of the catalytic reaction, the author used the same preparation method to synthesize catalysts with different supports (carbon nanotube, activated carbon, etc.) but the same Ru content and carried out the hydrogenation of LA under the same standard reaction conditions. The results showed lower reactivity toward the hydrogenation of LA with these catalysts, and the TEM characterization confirmed a certain degree of Ru NP aggregation when using CNTs or AC as the support (Figure 5). These results demonstrate that N-doped carbon materials are favorable for the uniform dispersion of metal species, which may also lower particle size and prevent metal species from aggregating, leading to higher atom utilization and a significant increase in catalytic activity.

Figure 4. The preparation procedure of Ru/HPNC catalysts. Reprinted with permission from Ref. [31]. Copyright © Elsevier Inc. 2022.
The catalytic transfer hydrogenation has attracted a great deal of interest as an alternative to direct hydrogenation since this strategy avoids the direct use of hydrogen, which makes it safer and less harmful to the environment. In recent years, transition metal anchored nitrogen-doped carbon catalysts have also made outstanding achievements in the transfer hydrogenation reactions. In 2021, Ma et al. successfully synthesized atomically dispersed Co catalysts by one-pot pyrolysis of bimetallic zeolitic imidazolate framework precursors (Figure 6) [32]. In the preparation procedure, Co$^{2+}$ ions might partially replace Zn$^{2+}$ and fabricate a bimetallic zeolitic imidazole framework by rebonding with 2-methylimidazole (ZnCo-ZIF). After carbonization, the single Co atoms anchored on N-doped carbon catalyst were synthesized. The obtained Co-N-C-900 catalysts were employed for the one-pot transfer hydrogenation of nitroarenes with saturated N-heterocycles as a hydrogen source in an aqueous solution, which exhibited excellent catalytic performance and was in line with the green and sustainable chemistry. A series of characterizations showed the single Co atom was banded with four nitrogen atoms in support to form a Co-N$_4$ active site. The density functional theory (DFT) calculations demonstrated the N atoms not only act as a coordinate site to trap Co single atoms but also play an important role in the transfer hydrogenation reaction (Figure 7). Based on the above research, the author concluded that the mechanism of transfer hydrogenation involved the production of H$_2$ from the dehydrogenation of 1,2,3,4-tetrahydroquinoline, which then worked as a source of hydrogen to reduce nitrobenzene. The resulted H$_2$ was absorbed on the Co-N$_4$ sites and dissociated to generate metal hydrides, which was the vital step for the whole catalytic loop. Then, hydrogen spillover proceeded from the Co atom to the N atoms and facilitated the formation of the N-H bond on the N-doped carbon matrix.

![Figure 5](image_url)  
**Figure 5.** Catalysts with different supports in the hydrogenation of LA. Reprinted with permission from Ref. [31]. Copyright © Elsevier Inc. 2022.

![Figure 6](image_url)  
**Figure 6.** Transfer hydrogenation reaction of nitroarenes with saturated N-heterocycles by Co-N-C-900 catalyst. Reprinted with permission from Ref. [32]. Copyright © Elsevier B.V. 2021.
which greatly boosted the reaction conversion.

Figure 7. DFT calculation for (a) the dehydrogenation of 1,2,3,4-tetrahydroquinoline and (b) the hydrogenation of nitrobenzene by Co-N-C-900 catalyst. Reprinted with permission from Ref. [32]. Copyright © Elsevier B.V. 2021.

3.2. Dehydrogenation Reaction

The dehydrogenation reactions are one of the most important reactions that are safer and more environmentally friendly than some direct oxidation reactions. The resulting hydrogen, as a by-product of the reaction, can be used as a fuel for further industrial applications. The transition metal anchored on N-doped carbon catalyst exhibited good performance in these types of reactions. In 2020, Dyson and colleagues disclosed core-shell nanocatalysts (Co-N/C-800) by encapsulating cobalt nanoparticles in a graphitic carbon shell, which were prepared by the in situ pyrolysis method of a cationic poly-ionic liquid with a cobalt precursor (Figure 8) [33]. The resulting catalyst displayed excellent catalytic performance in the self-dehydrogenation and hetero-dehydrogenation of primary amines to corresponding imines, and molecular hydrogen was the only byproduct released during the reaction. The core-shell structure of Co, N co-doped carbon catalysts greatly enhanced the selectivity of the dehydrogenation and the Co-N species acted as the main active sites, which greatly boosted the reaction conversion.

Figure 8. Selective acceptorless dehydrogenation of primary amines to imines by Co-N/C-800 catalyst. Reprinted with permission from Ref. [33]. Copyright © John Wiley & Sons 2020.

Chen’s group developed a Ni nanoparticle anchored on nitrogen-doped carbon-foam catalysts (Ni/NCF), which showed highly efficient and selective in the dehydrogenation reaction of gas-phase methanol to hydrogen and CO (Figure 9) [34]. Both theoretical and experimental results revealed the inductive effect of N atoms leads to a rise in the band gap of the nitrogen-doped carbon support. As a result, electrons were transferred from the Ni nanoparticles to the nitrogen-doped carbon support. With this loss of electrons, the
Ni nanoparticles had a stronger interaction with the O-H bond in the methanol, therefore accelerating the dehydrogenation reaction.

![Dehydrogenation reaction of methanol](image)

**Figure 9.** The dehydrogenation reaction of methanol by Ni/NCF catalysts. Reprinted with permission from Ref. [34]. Copyright © John Wiley & Sons 208.

In addition to nanoparticle-based catalysts, transition metal nanoclusters anchored on N-doped carbon also exhibited outstanding efficacy in dehydrogenation reactions. In 2021, Dong et al. reported a highly dispersed Co-cluster decorated N-doped carbon nanotubes catalyst (Co/N-CNTs) and employed it for the dehydrogenation of alcohols (Figure 10) [35]. The Co/N-CNTs catalysts were synthesized via a facile one-pot strategy with carbon nanotubes as a template, low-cost melamine, formaldehyde, and cobalt acetate as raw materials. The obtained Co/N-CNTs catalysts exhibited excellent catalytic performance in the dehydrogenation of various aliphatic alcohols and substituted benzyl alcohols under an inert atmosphere with water as a green solvent. These N species in the Co/N-CNTs catalyst acted as anchor sites for the nucleation and growth of Co clusters, as well as heterogenized ligands that accelerated the chemical activity and stabilized the Co active species. The aberration-corrected high-angle annular dark-field scanning transmission electron microscopy and synchrotron radiation characterization demonstrated that Co clusters were uniformly dispersed on the N-CNTs and the coordinated numbers of Co-Co and Co-N were 3.2 and 1.2, respectively. The DFT calculation of the reaction mechanism suggested the high atom utilization in metal clusters and the important role of N atoms for the benzyl alcohol dehydrogenation to the benzaldehyde, which was proved to be the rate-determining step in the entire catalytic cycle.

![Preparation procedure of Co/N-CNTs catalysts](image)

**Figure 10.** The preparation procedure of Co/N-CNTs catalysts. Reprinted with permission from Ref. [35]. Copyright © John Wiley & Sons 2021.
3.3. Oxidation Reactions

One of the most significant procedures for manufacturing numerous high-value compounds is selective oxidation, and the transition metal anchored on carbon catalysts doped with nitrogen has a variety of applications in this process. In the aerobic oxidation of alcohols, it is usually necessary to add a base to the reaction system, which helps to trap hydrogen ions from the hydroxyl groups of the reactants to initiate the reaction [36,37]. The utilization of nitrogen-doped carbon materials as a catalyst support in selective oxidation reactions may play a similar role to that of base additives.

Wang’s group synthesized Pt nanoparticles anchored on N-doped carbon catalysts (Pt/C-EDA-x) by a hydrothermal method using ethylenediamine as the nitrogen source (Figure 11) [38]. In agreement with the expected results, the reactivity of this catalyst in the selective oxidation reaction of 5-hydroxymethylfurfural (HMF) under base-free conditions was comparable to that of the non-nitrogen-doped carbon-supported Pt catalyst with the additional addition of base. On the basis of the CO$_2$-TPD results, the author found that the doping of nitrogen during catalyst preparation could introduce base sites in the carbon material. They further demonstrated that pyridine N could serve as a relatively strong basic site that improving catalytic activity under base-free conditions. In the oxidation of HMF, these basic sites on the surface of the catalyst can accelerate the synthesis of intermediate hemiacetals by promoting the activation of hydroxyl groups.

![Figure 11](image-url)

**Figure 11.** The selective oxidation reaction of 5-hydroxymethylfurfural (HMF) under base-free conditions by Pt/C-EDA-x catalyst. Reprinted with permission from Ref. [38]. Copyright © Elsevier B.V. 2016.

Besides, the doping of N atoms was beneficial to stabilizing and anchoring metal atoms, thus facilitating the preparation of single-atom catalysts. The isolated metal atom was coordinated with N atoms to give a M-N$_x$ active site in single-atom catalysts, which exhibited excellent activity in selective oxidation reactions. In 2022, Beller et al. developed isolated single iron atom catalysts anchored on N-doped carbon via one-step pyrolysis of benzylamine-modified zeolitic imidazolate framework (Figure 12) [39]. The obtained Fe$_1$-N-C catalyst was employed in the aerobic oxidation of diverse alcohols to synthesize various aryl, heterocyclic, allylic, and aliphatic nitriles with outstanding performance under very mild conditions. The reactions employed molecular oxygen as the only oxidant and aqueous ammonia as the nitrogen source, which greatly meets the demands of green and sustainable chemistry. The benzyl alcohol was directly oxidized to benzoaldehyde, and then the aldehydes were reacted with ammonia through dehydrative condensation, which resulted in the formation of imines, followed by the creation of benzonitrile.
3.4. Hydroformylation Reactions

Hydroformylation is a fundamental transformation in manufacturing applications that uses CO, H₂, and olefins to synthesize aldehydes. Due to their excellent catalytic activity and selectivity, homogeneous catalysts have been widely employed in this reaction throughout the last decade. However, the complicated synthesis of pincer ligands, limited recyclability, and durability of homogeneous catalysts severely limit their future applications. Thus, it is of great significance to develop high-performance and stable heterogeneous counterparts. Among many heterogeneous catalysts, the transition metal anchored on nitrogen-doped carbon catalysts have been widely noticed and utilized due to its excellent performance. In 2022, Corma et al. reported a heterogeneous ruthenium catalyst (Ru@NC) that is composed of isolated single atoms and disordered clusters supported in an N-doped carbon matrix (Figure 13) [41]. The synthesized catalysts showed excellent reactivity and outstanding regioselectivity in the hydroformylation of 1-hexene. Nitrogen has been shown to be crucial for both the formation and stability of Ru(II)-N active sites, which remain stable and without any sintering after several catalytic cycles.

For the preparation of the Fe-based catalyst, the addition of benzylamine served as an additive proved to be essential for the tuning of the morphology and size of the zeolitic imidazolate framework, which further led to stable and uniformly dispersed Fe active sites. The synchrotron radiation analysis of X-ray absorption near-edge structure (XANES) and the Fourier-transformed k³-weighted extended X-ray absorption fine structure (FTEXAFS) spectrum exhibited that single Fe atom was coordinated with four N atoms to form a Fe-N₄ site, which strongly suggested the N atoms in the N-doped carbon material could help stabilize the single atom site and thus enhance the catalytic activity and stability of the catalyst. It is noteworthy that N species serve a vital role in the catalyst’s preparation and catalytic reactions, by regulating the amount of nitrogen source in the synthesis process can significantly adjust the N contents of the catalysts. The adjustable nitrogen loading was able to effectively regulate the electron transfer from metal species to N atoms, and then to the N-doped carbon support. Recently, Shen et al. developed a single Fe atom catalyst (SA-Fe/Nₓ-C) based on N-doped graphitic carbon for the selective oxidation of benzyl alcohol to benzaldehyde [40]. The SA-Fe/Nₓ-C catalysts were synthesized by a ligand-coordinated metallic strategy with carbon nitride as template agent and nitrogen source. Additionally, the N content doped into carbon could be regulated by tuning the ratio of carbon nitride used in the preparation of catalysts. This successfully accomplished controllable adjustment of the electron transfer of metallic Fe and led to the electron deficiency of Fe atoms, which improved the selective benzyl alcohol oxidation.

Figure 12. The preparation procedure for Fe₁-N-C catalyst. Reprinted with permission from Ref. [39]. Copyright © Springer Nature 2022.
3.5. Electrocatalytic Reactions

With the worsening energy and environmental crisis, the search for clean and alternative energy sources has become a main consideration for the human society. One of the fundamental technologies for addressing the energy problem is electrocatalysis, which plays a significant role in energy storage and transformation systems. The most promising energy storage, transport, and conversion technologies are fuel cells, water splitting, and metal-air batteries, etc., which depend heavily on electrocatalytic processes such as hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), and oxygen evolution reaction (OER) [42]. Transition metals anchored on nitrogen-doped carbon with changed electronic structure, facilitated charge transfer, and high metal utilization have received a significant lot of attention and research in recent years as excellent electrocatalysts [43]. In this section, both theoretical and experimental advances in the catalytic application of ORR, OER, and HER are discussed.

3.5.1. Oxygen Reduction Reaction (ORR)

The ORR can generate an intermediate H$_2$O$_2$ (O$_2$ + 2H$^+$ + 2e$^-$ → H$_2$O$_2$) via a two-step pathway or a final product of H$_2$O (O$_2$ + 4H$^+$ + 4e$^-$ → 2H$_2$O) through a four-electron pathway, which is a critical process in fuel cells, metal-air batteries, and other applications [11]. Recent studies have focused on transition metal anchored on nitrogen-doped carbon catalysts for the ORR, since the doping of N atoms and transition metals considerably improves the electron-donating capacity and, consequently, the activity of the ORR [44]. As nitrogen contains one more electron and a stronger electronegativity than carbon, it prefers to take electrons from carbon, resulting in a partial positive charge on carbon and an increased interaction with O$_2$ [45]. Mu et al. developed a Pt nanoparticles supported on nitrogen-doped reduced graphene oxide (NRGO) catalyst that is used in proton exchange membrane fuel cells [46]. The obtained Pt/NRGO catalysts with uniform metal dispersion and high N content exhibited excellent performance in ORR. Compared with the catalysts without N doping (Pt/GO and Pt/C), Pt/NRGO catalysts exhibited not only higher ORR activity but also lower loss of electrochemical active surface area and better cycling stability. The N-atom doping considerably increased the electrical conductivity, dispersion, and size distribution of Pt NPs, which were responsible for the enhanced electoral activity and stability. Besides, the N-doped carbon support could serve as an assistant catalyst in ORR to further improve the catalytic performance.

This study demonstrated the potential for transition metal anchored on nitrogen-doped carbon catalysts to be used in fuel cells. Due to the extraordinary performance of nitrogen-doped carbon in the construction of single-atom catalysts, a growing proportion of single-atom catalysts with superior performance have been used for this reaction. Recently, Li et al. developed a dopamine-assisted synthesis and ammonia activation method for the fabrication of cobalt-based single-atom N-doped carbon electrocatalysts (Co SAs/NC) with particular morphology, size, and electronic structure (Figure 14) [47]. The Co SAs/NC...
catalyst possessed an abundance of easily accessible active sites and a large electrochemically active area, which resulted in good catalytic activity in alkaline ORR reactions with onset and half-wave potentials of 1.04 V (RHE) and 0.90 V (RHE), much higher than other comparable catalysts and superior to the majority of previously reported non-precious metal alkaline ORR electrocatalysts. According to experimental and theoretical results, the Co-N sites greatly enhanced the adsorption/desorption of oxygen intermediates and further promoted the reaction kinetics. Furthermore, the DFT calculation revealed that the positive valence states of Co atoms contributed to the charge transfer between Co and N atoms, which drastically improved the electrocatalytic activity for ORR.

Figure 14. ORR by the Co SAs/NC catalyst with rich active Co sites. Reprinted with permission from Ref. [47]. Copyright © Elsevier B.V. 2022.

3.5.2. Hydrogen evolution reaction (HER)

HER is a significant method for producing hydrogen energy by electrochemical water splitting. This procedure involves a two-electron transfer reaction that follows either the Volmer-Heyrovsky mechanism \((H^+ + e^- \rightarrow H_{ads}, H_{ads} + H^+ + e^- \rightarrow H_2)\) or Volmer-Tafel mechanisms \((H^+ + e^- \rightarrow H_{ads}, H_{ads} + H_{ads} \rightarrow H_2)\) [48]. The kinetics of both processes are determined \((\Delta G_{H_{ads}})\) by the free energy of hydrogen adsorption [49]. The transition metal anchored on nitrogen-doped carbon catalysts with a low absolute \(\Delta G_{H_{ads}}\) value could facilitate charge transfer as well as the formation and desorption of \(H_2\). As a consequence, these catalysts are seen to be the best choices for the HER. Hu et al. reported a single Pt atom anchored on hierarchical nitrogen-doped carbon nanocages catalyst (Pt/hNCNC) via a simple impregnation-absorption method [50]. The Pt/hNCNC catalyst outperformed Pt-based electrocatalysts without N dopant (Pt/hCNC) in terms of HER performance owing to its low overpotential, low Tafel slope, and long stability. The DFT calculation indicated the Pt-N bonds were more stable than Pt-C bonds, leading to the higher stability for the Pt/hNCNC than the Pt/hCNC in the HER process.

In 2022, Zhu group created single-atom electrocatalysts by anchoring a single Co atom to the g-C\(_3\)N\(_4\)/rGO support; the resulting Co-CNG catalysts had exceptional HER performance, even comparable to commercial Pt/C catalysts [51]. The N-doped carbon support enhanced the electrical conductivity of the catalytic system, firmly anchored the active sites, and facilitated a more uniform dispersion of metal species. According to the EXAFS results, the Co atom had two coordinate formations with N atoms, including Co-3N and Co-N, which served as the catalytic activity center in HER. The DFT research demonstrated the Co-N sites had a lower free energy of water cleavage and a suitable proton binding energy in comparison with the Pt (111) surface in commercial Pt/C catalyst, which is the essential reason for the high catalytic activity of Co-CNG catalysts. This work demonstrated that Co-CNG catalysts were superior to commercial Pt/C catalysts for HER due to their unique single-atom coordination with N atoms, which facilitated the rational design of transition metal catalysts anchored on nitrogen-doped carbon for electrocatalysis.
3.5.3. Oxygen Evolution Reaction (OER)

OER, which is driven on the cathode surface of rechargeable metal-air batteries and water electrolysers, is an essential component of renewable energy conversion processes [43]. The OER is accomplished via a combination of four proton-coupled electron transfer mechanisms, and the process depends on the acidity or basicity of the reaction conditions (Acidic conditions: \(2\text{H}_2\text{O} \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^-\); Alkaline conditions: \(4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-\)) [52]. By developing highly-efficient transition metal anchored on nitrogen-doped carbon catalysts, it is capable of producing a remarkable OER performance. Recently, Chen et al. synthesized a Ni, N co-doped 3D nanoporous graphene catalyst that showed outstanding electrocatalytic activity for OER in alkaline aqueous solutions [53]. The synergetic effects of N and Ni atoms improved intermediate stability and lowered free energy, resulting in a high OER performance. Fei et al. investigated OER activity and mechanism employing three different single metals anchored on N-doped graphene catalysts (Fe, Co, and Ni) to determine the relationship between atomistic structure and catalytic characteristics [54]. The experiments and DFT analysis showed that the main active site was MN_4N_4 (M = Fe, Co, and Ni), and the OER performances followed the trend of Ni > Co > Fe. With an overpotential of \(\sim 331\) mV, Ni-based catalysts had the highest OER activity compared to the other two catalysts. In addition, theoretic studies indicated that N atoms and adjacent C atoms could serve as assist catalytic active sites to improve reactions at Ni centers.

4. Summary and Future Outlook

In this review article, we summarized the recent breakthroughs in the fabrication procedures of transition metal anchored on nitrogen-doped carbon catalysts as well as prospective applications in diverse organic reactions and electrocatalysis. The doping of nitrogen atoms significantly regulates the physicochemical properties of the pristine carbon material and enhances the interaction between the transition metal active species and support, changing the electronic structure of the metal active sites and providing them with an abundant anchor position, resulting in better catalytic performance and stability of the catalysts. Even if remarkable progress has been achieved in the catalytic transformation of organic compounds over transition metals anchored on nitrogen-doped carbon as thermocatalysts and electrocatalysts, the continued research and practical application of transition metals anchored on nitrogen-doped carbon catalysts requires dedicated research and innovation.

First, the extremely high surface energy of transition metal atoms makes them prone to aggregation into large nanoparticles during catalyst preparation and reaction. This issue generally results in lower atomic utilization and uneven dispersion on the support, finally resulting in a considerable decrease in catalyst activity. Thus, establishing the flexible size and robust metal active sites is one of the critical problems that needs to be further studied in transition metals anchored on nitrogen-doped carbon catalysts. Second, it is highly essential to elucidate the structural characteristics and reaction mechanism of transition metals anchored on nitrogen-doped carbon catalysts that influence the catalytic activity. Besides, the understanding of the relationship between the N-doped carbon support and transition metal sites needs further improvement, which will help researchers to design more effective catalysts for specific catalytic reactions. Third, the obstacles in the scalable and controllable synthesis of high catalytic performance and thermostable transition metals anchored on nitrogen-doped carbon catalysts remain to be addressed. The development of simple, cost-effective, and structurally flexible catalyst preparation methods is still necessary for large-scale applications. Finally, the advanced characterization and calculation techniques for both the catalysts and reactions should also be developed in order to get a comprehensive understanding of the relationship between the characteristics of the nitrogen species and the catalytic properties of the corresponding catalysts, which may provide more insight for the reaction mechanism and the evolution of catalysts.
In conclusion, despite the fact that transition metals anchored on nitrogen-doped carbon catalysts have been shown to be effective in various catalytic processes, it is still a long way from large-scale application in industrial production, and there are still many challenges for the study of the relationship between active sites and nitrogen-doped carbon support in catalysts. As such, the precise design and large-scale industrial applications of transition metal anchored on nitrogen-doped carbon catalysts still need to be further studied. This review is expected to inspire the future synthesis and application of promising transition metals anchored on nitrogen-doped carbon catalysts.

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