Transition Metal Anchored on Nitrogen-Doped Porous Carbon Catalysts

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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. 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.

nitrogen-doped porous carbon support | metal catalyst | heterogeneous catalysis

1. 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. [1]. **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. Post-Loading Method

In the past decades, the post-loading method has prepared most of the transition metals anchored on N-doped carbon catalysts [2][3][4]. 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 [3]. 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. Impregnation Method

Impregnation is an efficient and straightforward method for the synthesis of heterogeneous catalysts and is widely utilized in industrial catalyst preparation [4]. 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 [5]. First, a certain amount of $Co(OAc)_2 \cdot 4H_2O$ and [MCNIm]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 [6].

2.2. 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 [7]. 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 [8]. 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.

3. 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 [9]. 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.

4. 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 [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.

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