Abstract
Ultrasmall metal nanoparticles (MNPs) and atomically dispersed metal sites (ADMSs) exhibit excellent catalytic activity and selectivity. However, they tend to aggregate into large particles during synthesis and catalysis due to high surface free energy. Aiming to break out of this dilemma, zeolite imidazolate frameworks (ZIFs) have proved to be ideal substrates for stabilizing the ultrafine metal nanostructures. The stabilizing mode includes confining MNPs inside their pore structures and converting intrinsic metal nodes into coordinately unsaturated metal sites (i.e., ZIF-confined metal catalysts). Furthermore, various MNPs and ADMSs can also be immobilized into ZIF-derived porous carbon through high-temperature pyrolysis (i.e., ZIF-derived carbon-supported metal catalysts). In brief, ZIFs and their derivatives have gradually emerged as good platforms for designing metal catalysts at nanoscale and even atomic level. In this review, recent progress in the structural analysis and synthetic strategies of metal catalysts supported by ZIFs and their derivatives is presented. Besides, current challenges and future directions of atomically dispersed metal catalysts are discussed. This article will provide valuable insights into rational design of metal catalysts with exquisite nanostructure and high catalytic performance to meet further material requirements in the catalytic field.

KEYWORDS
single-atom catalysts, synthetic strategy, ultrasmall metal nanoparticles, zeolite imidazolate frameworks, ZIF-derived carbon

1 | INTRODUCTION
Catalysts have been broadly used in modern society, such as energy conversion, chemical production, and environmental protection.[1–7] Rational selection and fabrication of high-performance catalysts have always been the frontier of scientific research. Attribution to the development of nanoscience, considerable nanocatalysts with ingenious structures are continuously fabricated and refresh people's understanding of catalysis. Among all existing nanocatalyst systems, metal catalysts have received more attention because of their high activity,
facile structural design, and good durability.\cite{8} Previous studies on metal nanocrystal catalysis have demonstrated that the size of metal particles significantly impacts the catalytic activity and selectivity, which often show distinct responses to target chemical reaction, for instance, catalytic, inert or even biased to trigger side reactions.\cite{8–11} This is due to the properties of metal atoms located on the surface of MNPs, such as electronic structure, oxidation state, and unsaturated coordination, varying with particle size. Based on these understandings, downsizing MNPs is beneficial to improve the percentage of surface metal atoms and optimize the unsaturated coordination of surface metal sites. Further, preparing MNPs with the uniform size is an effective way to improve catalytic selectivity.\cite{11–14} Benefiting from advances in synthetic methodology of nanomaterials, researchers have been able to manipulate metal species ranging from nanoparticle to atom in recent years.\cite{15,16} Especially, atomically dispersed metal sites (ADMSs) exhibit high metal atom utilization efficiency (conceptually 100%) and excellent catalytic performance.\cite{15,17,18} However, a common challenge for these small-sized metal species is the dramatically elevated surface free energy, which could induce severe aggregation during catalytic process.\cite{16} Hence, porous supporters’ selection for stabilizing small-sized metal species has become the key to improve durability of nanocatalysts.\cite{19–21}

Zeolite imidazolate frameworks (ZIFs), constructed from transition metal ions and imidazolate linkers, have attracted much attention since their emergence. ZIFs have a similar structure to aluminosilicate zeolites, where metal ions and imidazole occupy silicon (aluminum) and oxygen, respectively. Thus, ZIFs concurrently maintain the structural characteristics of metal-organic frameworks (MOFs) and zeolites, such as high surface area, great structural tailorability, zeolite-like topologies and high stability.\cite{22–24} ZIFs possess well-defined pore structures and uniform aperture distribution. It should point out that the pore size of ZIFs is at molecular scale. The pore size between cavities (diameter: 11.6 Å) of ZIF-8 is 3.4 Å, which is at the molecular scale.\cite{22} This is also supported by some application studies that molecular-scale pores of ZIF materials can selectively separate gas molecules with different sizes by blocking the passage of gas molecules with a diameter larger than aperture.\cite{25,26} In recent years, ZIFs are directly applied to incorporate small-sized metal species (MNPs less than 5 nm and ADMSs) into their pore spaces (Figure 1A).\cite{27,28} Application of ZIFs as host matrix is mainly based on the following advantages: first, ultrasmall MNPs, and ADMSs can be well fabricated and stabilized.

**FIGURE 1** Metal catalysts supported on ZIFs and ZIF-derived nitrogen-doped carbon. A, ZIF-confined metal catalysts (metal nanoparticles and atomically dispersed metal sites). Reproduced with permission.\cite{27,28} Copyright 2011, American Chemical Society; Copyright 2019, Wiley-VCH. B, ZIF-derived carbon-supported metal catalysts (metal nanoparticles and atomically dispersed metal sites). Reproduced with permission.\cite{35,36} Copyright 2015, American Chemical Society; Copyright 2020, Wiley-VCH.
within ZIF frameworks; second, size-selective catalysis (reactants that are smaller than apertures can enter interior of ZIFs to interact with catalytically active sites, while larger ones are excluded) is realizable based on molecular-scale pores of ZIFs; third, catalytic performance is significantly enhanced because of synergistic effect between MNPs and ZIFs.\[^{29,30}\]

Further, in high-temperature pyrolysis under controlled atmosphere (e.g., H\(_2\), Ar, N\(_2\), or NH\(_3\)), ZIFs are converted into nitrogen-doped carbon materials.\[^{31-34}\] Derived nitrogen-doped carbon materials possesses the following characteristics: (1) high porosity and surface area allow fast mass diffusion in catalytic reactions; (2) interconnected carbon skeleton possesses good electrical and thermal conductivity; (3) differing from other doping methods, nitrogen in imidazolate linkers can be in situ incorporated into carbon frameworks during high-temperature pyrolysis, thus creating suitable microenvironment for stabilizing intrinsic/foreign metal species; (4) the structural tailorability of precursor ZIFs gives inherent vitality to the innovation of ZIF-derived carbon materials. As shown in Figure 1B, ZIF-derived nitrogen-doped carbon has been demonstrated that it is suitable supporters for stabilizing metal species ranging from nanoparticles to ADMSs.\[^{35,36}\] Notably, nitrogen sites in ZIF-derived carbon play a key role in anchoring metal species, especially anchoring ADMSs, because of the strong coordination between nitrogen and metal.\[^{19,37,38}\]

Naturally, ZIF-confined metal catalysts and ZIF-derived carbon-supported metal catalysts have stimulated much interest in catalysis fields. Recent progress in catalytic applications of ZIF-confined MNPs (synergistic effect between MNPs and ZIFs in catalysis) has been comprehensively reviewed by Jiang et al.\[^{39}\] Some reviews have also summarized electrocatalytic applications (e.g., oxygen reduction reaction in fuel cells) of ZIF-derived nanocatalysts, including MNPs and single-atom catalysts.\[^{32-34}\] The strong structural correlation between ZIFs and ZIF-derived carbon essentially determines that ZIF-confined metal catalysts and ZIF-derived carbon-supported metal catalysts have similarities in design and synthesis. However, only a few reviews integrate synthetic strategies and structural characteristics of these supported metal catalysts. Accordingly, this review emphasizing integration for synthetic strategies and underlying structural basis of the above two catalysts will provide valuable guidance for further material design at nanoscale and even atomic level. Recently, a review named “Integration of Metal Nanoparticles into Metal-Organic Frameworks for Composite Catalysts: Design and Synthetic Strategy” was published by Cheng et al. It covered the main synthetic strategies of MOF-confined MNPs.\[^{39}\] In contrast, we give a focused summary of the synthesis of metal catalysts with ZIF and ZIF-derived carbon as supporters and simultaneously take into account the architectural design of ADMSs (single-atom, dual-atom, and triatomic cluster catalysts) in this review. Meanwhile, compared with MOF-based single/dual-atom and cluster metal catalysts comprehensively reviewed by Xu and co-workers, this review focuses on discussing ZIF-based MNPs and ADMSs to localize synthesis issues into ZIF materials (one class of MOFs), thus to reveal the chemical mechanism behind synthetic strategies more clearly.\[^{40}\]

In this review, the design and synthetic strategies of metal catalysts supported on ZIFs and their derivatives are classified and summarized from nanoparticles to ADMSs. Logically, our discussion starts from structural analysis of ZIFs and ZIF-derived nitrogen-doped carbon materials. After that, advanced synthetic strategies of ZIF-confined metal catalysts are described based on two metal species: nanoparticles, and ADMSs. Hopefully, this timely review aims to provide the readers with a comprehensive overview and deep understanding of the chemical synthesis of emerging metal catalysts using ZIFs and their derivatives as design platform.

2. STRUCTURAL ADVANTAGES OF ZIFS AND ZIF-DERIVED CARBON

2.1 Structural advantages of ZIFs

2.1.1 Structural characteristics of ZIFs

The characteristic M-Im-M moieties of ZIFs are constructed by self-assembly of tetrahedrally coordinated transition metal ions (M) and imidazolate (Im). As shown in Figure 2A, since the M-Im-M bonding angle is consistent with Si-O-Si angle (145°) of aluminosilicate zeolites, ZIFs tend to form zeolite-like structures. Therefore, they are considered as zeolite analogues, in which metal ions and imidazolate respectively occupy the positions of silicon (aluminum) and oxygen.\[^{22-24}\] In summary, ZIFs integrate structural characteristics of metal-organic frameworks and conventional zeolites. ZIF structures have great tailorability, that is, metal nodes and imidazolate linkers in structures are both modifiable. Based on the structural tailorability, hundreds of ZIF structures have been synthesized by altering kinds of metal ions and imidazolate or controlling reaction conditions. In 2010, Yaghi and co-workers classified these ZIF structures according to topological type, and results showed that some ZIFs possess traditional zeolite topologies (Figure 2B).\[^{24}\] Another example of structural tailorability is that the post-synthetic modification by introducing
chemical reagents into as-synthesized ZIFs can covalently functionalize imidazolate linkers to satisfy idiographic application requirement (Figure 2C).\[41\]

In addition to structural tailorability, ZIFs display high chemical and thermal stability due to strong metal-nitrogen bonds in M-Im-M moieties. Experiments of Yaghi’s group showed: ZIF-8 could maintain crystalline structures when suspended in boiling water, boiling methanol, and boiling benzene for 7 days; ZIF-8 remained unchanged in sodium hydroxide aqueous solution at 100 °C for 24 hours.\[22\] Furthermore, the ZIFs possess well-defined pore structures and are readily prepared in laboratory.\[42,43\] For example, crystalline ZIF-8 with sodalite (SOD) topology can be readily synthesized by stirring mixed methanol solutions of metal ions and imidazolate at room temperature.\[42\]

2.1.2 Pore confinement effect

As a class of porous nanomaterials, ZIFs were applied in gas separation (H₂, CO₂, etc.) in earlier years because of their molecular-scale pores.\[25,26\] Benefiting from these advances, scientists have a comprehensive understanding of ZIF pore structure properties and then seek more applications. Up to now, numerous facile designs have been proposed for metal catalysts based on the pore confinement effect of ZIFs. Whether ZIF-confined metal catalysts or ZIF-derived carbon-supported metal catalysts, their synthetic processes are more or less dependent on confinement effect of ZIF pore structures. Regarding the synthesis of ZIF-confined metal catalysts, molecular-scale pores of ZIFs influence the immobilization of ultrasmall MNPs and ADMSs. High surface free energy induces severe aggregation of metal species to form large particles during the reduction process of metal precursors to zero-valent metal species. If these metal precursors are well confined into ZIF matrix, aggregation can be significantly inhibited, and metal species are forced to form ultrasmall nanoparticles.\[27,29,30,44,45\] Meanwhile, atomically dispersed metal catalysts have also been successfully constructed based on specific metal precursors confined into ZIF pore structures.\[28\] On the other hand, the pore confinement effect of ZIFs is also essential for fabricating carbon-supported metal catalysts. For example, molecular-scale cages of ZIF-8 have been used to encapsulate suitable metal precursors to form metal single-atom catalysts after pyrolysis. One-to-one encapsulation of single metal precursors by each ZIF cavity is key in “spatial confinement strategy”.\[46–49\]

2.2 Structural advantages of ZIF-derived carbon

2.2.1 Structural characteristics of ZIF-derived carbon

Generally, the imidazolate linkers of ZIFs are transformed into nitrogen-doped carbon frameworks (amorphous
carbon or graphitic carbon) and metal nodes are converted into corresponding metals or metal oxides depending on their own reduction potential during high-temperature pyrolysis.\cite{31–35,50–53} Such pyrolysis process has been widely adopted for synthesizing carbon-supported metal nanoparticle catalysts and even atomically dispersed metal catalysts.\cite{35,52}\footnote{For the final catalyst structures, ZIF-derived carbon materials as host determines the stability of metal species and may be involved in the evolution of active catalytic sites, such as nitrogen-coordinated metal sites (M-N_x).\cite{52} Overall, the structural characteristics of ZIF-derived carbon materials are worthy of analysis in detail. Herein, the discussion on structural characteristics highlights general characteristics inherited from ZIFs, bonding configurations of nitrogen doping and structural differences resulting from different ZIFs.}

2.2.2 General characteristics inherited from ZIFs

Like most derivatives, derived nitrogen-doped carbon inherits some structural characteristics of parent ZIFs. Although ZIF frameworks undergo partial destruction and shrinkage at high temperature, derived nitrogen-doped carbon still retains high surface area and porosity. Liu et al. reported the first attempt of using cobalt imidazolate frameworks as precursors for the synthesis of carbon-supported cobalt catalysts.\cite{53} Brunauer-Emmett-Teller (BET) specific surface area (SSA) of precursor cobalt imidazolate frameworks was 305 m²g⁻¹ and micropores with dimensions ranged from 8 to 13 Å in their characterization. While derived carbon-supported cobalt catalysts retained good BET SSA of 264 m²g⁻¹ and formed many micropore and mesopore regions after thermal treatment at 750 °C. Similarly, Ren and co-workers reported a cobalt and nitrogen-doped carbon (CoNC) electrocatalyst prepared by direct carbonization of ZIF-67.\cite{31} Their work indicated that ZIF-67 was converted into CoNC frameworks with more micropores and some mesopores. In summary, ZIF-derived nitrogen-doped carbon exhibits micro/mesoporous structures and high surface area inherited from ZIF materials.

2.2.3 Bonding configurations of nitrogen doping

Nitrogen of imidazolate linkers is in situ incorporated and uniformly dispersed into carbon matrix at high temperature. As is well known, bonding configurations of nitrogen doping within conventional graphitic networks are pyridinic, pyrrolic, graphitic (quaternary) N, and pyridinic N-oxide.\cite{19,20,54}\footnote{These nitrogen sites are also present in ZIF-derived nitrogen-doped carbon materials. As shown in Figure 3A, pyridinic N species are generally incorporated into the hexagonal rings and located at edges or in vacancies of graphitic networks. Pyrrolic N species are inserted into the pentagonal rings of graphitic networks and graphitic N refers to these nitrogen atoms that replace carbon atoms in graphite plane. It must mention that above bonding configurations of nitrogen only stand for carbon-nitrogen interaction. Researchers conjecture that metal-nitrogen interaction (i.e., nitrogen-coordinated metal species) also exist in some ZIF-derived carbon-supported metal catalysts. In 2011, when analyzing carbon-supported cobalt catalysts derived from cobalt imidazolate frameworks after acid leaching, Liu and co-workers first observed the spectroscopic characteristics of Co-N_x.\cite{53} Another study of the same group also showed that iron-based catalysts derived from iron imidazolate frameworks might involve Fe-N_4/C or Fe-N_2/C as catalytic sites.\cite{55}\footnote{In 2016, Li and co-workers pioneered the synthesis of single atom cobalt catalysts using bimetallic Zn/Co ZIFs. In their research, atomically dispersed cobalt sites with precise N-coordination (Co-N_x) were clearly identified by X-ray absorption fine structure (XAFS) and high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM).\cite{52} Since then, various ZIF-derived carbon-supported single-atom metal catalysts (Fe, Cu, Ni, Rh, Pt, Ir, etc.) have been reported.\cite{36–38,46,49,56–59} These research efforts suggest that metal-nitrogen interaction exist extensively in ZIF-derived carbon-supported metal catalysts.}

2.2.4 Structural differences resulting from different ZIFs

Besides, precursor ZIFs have a significant impact on final graphitization degree, surface area, micro/mesoporous nature, and overall N content. The precursor of ZIFs selected for carbonization is mainly divided into two categories: Zn-containing ZIFs (ZIF-8, ZIF-7) and Co-containing ZIFs (ZIF-67, ZIF-9). Different metal nodes influence the evolution trend of ZIFs at high temperature. During the carbonization of Zn-containing ZIFs, zinc ions can be reduced to metallic zinc by surrounding carbon and gradually evaporated at high temperature to obtain metal-free nitrogen-doped carbon (boiling point of metallic Zn is 907 °C). Nevertheless, for the carbonization of Co-containing ZIFs, reduced cobalt species are incorporated into nitrogen-doped carbon frameworks because they cannot be evaporated at carbonization temperature and behaved as graphitizing catalysts to improve the degree of graphitization of carbon further.\cite{33,50,60}
To analyze the detailed structural differences caused by different metal nodes (zinc and cobalt), researchers chose Zn-containing ZIF-8 and isostructural Co-containing ZIF-67 for respective calcination under the same carbonization conditions. Results showed that nitrogen-doped carbon derived from ZIF-8 is essentially amorphous carbon with high nitrogen content and high surface area. And it exhibits abundant structural defects resulting from Zn evaporation but low graphitization and poor conductivity. In comparison, ZIF-67 derivatives are generally cobalt-containing graphitic carbon with high conductivity but low nitrogen content and low surface area. In order to combine the advantages of both, Jiang and co-workers selected bimetallic Zn/Co ZIFs (BMZIFs) as precursor for pyrolysis. As shown in Figure 3B, prepared Co, N-doped porous carbon catalysts not only had high nitrogen content and large surface area, but also exhibited good graphitization and involvement of Co nanoparticles. Almost simultaneously, Sun’s group also found that Co, N-doped porous carbon catalysts derived from bimetallic ZIFs showed excellent catalytic activity due to the large surface area, high nitrogen content (similar to carbonized ZIF-8) and small Co nanoparticles interacted with N (similar to carbonized ZIF-67). Accordingly, types of precursor ZIFs have become a controllable parameter for optimizing derived carbon structures.

2.2.5 | Anchoring metal species through nitrogen sites in ZIF-derived carbon

Early studies suggested that heteroatom doping (nitrogen) could change the intrinsic structures of carbon materials and influence MNPs supported on nitrogen-doped carbon: (1) nitrogen in carbon matrix can serve as anchoring sites for the nucleation, growth and highly uniform dispersion of MNPs; (2) MNPs supported on nitrogen-doped carbon are more stable due to strong binding energy between metal and nitrogen sites; (3) nitrogen doping influences electronic and geometric structures of MNPs due to charge transfer of metal-support interface and lattice mismatch between the carbon matrix and MNPs. Recently, with the development of ZIF-derived single-atom M-Nₓ catalysts, scientists have more understanding of anchoring metal species through nitrogen sites from atomic perspective. Typically, in
ZIF-8-derived nitrogen-doped carbon, abundant nitrogen sites (pyridinic N and pyrrolic N) are generated due to zinc evaporation. These active nitrogen species can anchor mobile metal atoms and even split metal atoms from MNPs at high temperature. In conclusion, active nitrogen sites in ZIF-derived carbon materials play an important role in the immobilization of metal species.

3 SYNTHESIS OF ZIF-CONFINED METAL CATALYSTS

3.1 Synthesis of ZIF-confined metal nanoparticle catalysts

In recent decades, metal nanoparticle catalysts have been extensively studied due to their superior activities. Researchers gradually found that the size of MNPs is a key factor affecting catalytic performance. As the particle size decreases, small MNPs generally exhibit enhanced activity but are prone to aggregate because of high surface free energy. In order to obtain highly stable catalysts, specific porous materials, for example, MOFs and porous carbon, have been selected as hosts to confine these MNPs into their void pores. This methodology has several main advantages: (1) Obtaining MNPs with ultrasmall size in synthetic process based on pore confinement effect, and (2) avoiding direct exposure of MNPs to cruel reaction conditions in catalytic process. Recently, ZIFs with well-defined pore structures have been developed as hosts to confine guest MNPs into their frameworks and prevent aggregation in catalytic process. ZIF pore structures characterized by large cavities and small pores not only spatially confine active MNPs but also are favorable for size-selective catalysis. Nevertheless, narrow pores also hinder desired MNPs from entering ZIF interior during synthetic process, thus placing tight requirements on synthetic methods. Herein, two main synthetic strategies for ZIF-confined metal nanoparticle catalysts are concluded: (1) postsynthesis strategy based on the preformed ZIFs, (2) encapsulation strategy during ZIF crystallization.

3.1.1 Postsynthesis strategy based on the preformed ZIFs

In this synthetic system, preformed ZIFs are base materials for subsequent operations. Metal precursors are infiltrated into preformed ZIFs and then reduced to MNPs. In short, postsynthesis means that the crystallization of ZIFs takes precedence over the formation of MNPs. Postsynthesis is mainly classified into three types as described below: impregnation, chemical vapor deposition, and solid grinding methods.

3.1.2 Impregnation method

Impregnation method is simple for the synthesis of ZIF-confined metal nanoparticle catalysts. In the impregnation process, the preformed ZIF crystals are mixed with a solution containing metal precursors. And the capillary pressure will force solution containing metal precursors to fully infiltrate into pore structures. Subsequently, reduction approaches are carefully employed to convert metal precursors into zero-valent MNPs without destroying the ZIF matrix. Because metal precursors are inevitably adsorbed on outer surface of ZIFs, the selection of metal precursors matching apertures of ZIFs and reduction conditions are key factors to obtain MNPs confined into the ZIF matrix. Small inorganic metal salts (e.g., HAuCl₄, AgNO₃, or K₂PdCl₄) are often used for impregnation because they are unobstructed within channels of ZIFs, whereas, metal complexes with larger diameter are generally not used for impregnation. As shown in Figure 4A, Shi’s group also demonstrated that Au25(SG)₁₈ (Au25 clusters protected by surface thiolate ligand glutathione [SG]) with large size of 15 Å could not pass through ZIF-8 micropores (3.4 Å). And they were therefore adsorbed on outer surface of ZIF-8 to form Au25(SG)₁₈/ZIF-8 during impregnation process. On the other hand, ultrahigh chemical stability of ZIFs gives more choices for reduction conditions. Metal precursors immobilized into ZIFs can be reduced to MNPs by NaBH₄ solution. Li’s group successfully incorporated rhodium nanoparticles into ZIF-8 via impregnation method. The preformed ZIF-8 was added to the solution containing RhCl₃ and then reduced with NaBH₄ solution. In obtained catalysts, Rh nanoparticles showed high dispersion in ZIF frameworks and even distribution in size due to pore confinement effect. Similarly, highly dispersed Pd nanoparticles embedded into ZIF-8 were also prepared via the impregnation method, in which Pd nanoparticles were found to be 2–3 nm. In addition to monometallic nanoparticles, ZIF-confined bimetallic nanoparticles can also be fabricated via the impregnation method. In 2011, Xu’s group successfully synthesized bimetallic Au@Ag core-shell nanoparticles with 2–6 nm via a sequential impregnation-reduction process (Figure 4B). HAUcl₄ and AgNO₃ were impregnated into ZIF-8 and then reduced by NaBH₄ to yield Au@Ag core-shell nanoparticles. Other ZIF-confined bimetallic nanoparticle catalysts were also successfully fabricated by impregnation method.
3.1.3 | Chemical vapor deposition method

Gas-phase chemical vapor deposition (CVD) is another effective method to obtain ZIF-confined metal nanoparticle catalysts. In CVD process, volatile organometallic compounds and desolvated ZIFs are placed in two separate glass vials in a Schlenk tube and then kept static under vacuum. Such manipulation allows the diffusion of volatile metal precursors into the ZIF matrix and then desired MNPs are obtained by subsequent H2 reduction. In CVD process, metal precursors are diffused into ZIF channels driven by vapor pressure. In 2012, Xu and co-workers synthesized nickel nanoparticles incorporated into ZIF-8 (CVD-Ni/ZIF-8) using CVD method (Figure 4C).[44] The small molecule nickelocene (Ni(cp)2) was selected as suitable volatile metal precursor to finally obtain nickel nanoparticles with mean diameter of 2.7 ± 0.7 nm. The crystalline structure of ZIFs was maintained well during CVD and H2 reduction process. Similarly, another volatile Ir(COD)(MeCp)((methylcyclopentadienyl)(1,5-cyclooctadiene)iridium) was also used for the synthesis of Ir nanoparticles within ZIF-8. The final Ir nanoparticles were restricted to 3.3 ± 1.7 nm by the microporous structures of ZIF-8.[68] In 2015, Liang’s group successfully synthesized Pd-based heterogeneous catalysts by vapor deposition of Pd(C6H5)(C2H4).[69] They observed that Pd nanoparticles with 1.5–3.0 nm were uniformly dispersed throughout the volume of ZIF-8.

3.1.4 | Solid grinding method

Utilizing volatile organometallic compounds, solid grinding method is another facile way to introduce metal nanoparticles into preformed ZIFs. During solid grinding process, the sublimated vapor of organometallic compounds can be immersed into ZIF matrix without vacuum condition. Such metal precursors embedded in ZIFs can be converted into small MNPs via H2 reduction at appropriate temperature. Examples are rare, but solid grinding is indeed an effective approach as reported by Xu’s group.[70] In their synthesis, ZIF-8 and (CH3)2Au(acac) (acac represents for 2,4-pentanediionate) were mixed and ground evenly in an agate mortar and then treated with gas containing H2 to produce Au@ZIF-8 with different Au content. Remarkably, the diameter of Au nanoparticles in Au@ZIF-8 was 3.4 ± 1.4 nm and nanoparticles were even miniaturized to 3.1 ± 0.9 nm after catalytic reaction due to restrictive role of ZIF pore structures. These developments indicate that MNPs confined into ZIF matrix can be effectively synthesized via solid grinding method.

3.1.5 | Encapsulation strategy during ZIF crystallization

Encapsulation is another synthetic strategy for ZIF-confined metal nanoparticle catalysts. In contrast to postsynthesis, encapsulation strategy emphasizes early control
over the size, shape, and composition of MNPs. Next, these preformed MNPs are added to ZIF synthetic solutions and then incorporated into ZIF matrix during crystallization process. In short, encapsulation means that the formation of MNPs takes precedence over the crystallization of ZIFs. Nonetheless, some difficult points exist in the encapsulation process, such as severe aggregation between metal nanoparticle individuals and phase separation between the ZIF matrix and MNPs. In order to stabilize these MNPs and improve their surface affinity with ZIF matrix, the metal-stabilizing reagents coated onto the surface of MNPs are required.[29,30]

In 2012, a controlled encapsulation strategy was conceived to confine MNPs into ZIF-8 crystals.[45] MNPs were first stabilized by polyvinylpyrrolidone (PVP) surfactant, and then PVP-stabilized nanoparticles were adsorbed onto the continuous forming surfaces of the growing ZIF-8. In their experiment, ultrasmall Pt nanoparticles with size of 2.5, 3.3, and 4.1 nm had been effectively encapsulated into ZIF-8 frameworks. Such encapsulation strategy based on PVP-stabilized nanoparticles had been widely applied for immobilization of noble metal nanoparticles in ZIF matrix.[71–73] In addition to PVP, other surfactants such as quaternary ammonium surfactants (CnTA) can also functionalize the surface of MNPs to improve their interaction with ZIFs.[74,75] As shown in Figure 5A, Tsung’s group developed an encapsulation strategy to bridge the surfaces of Pd nanocube and ZIF-8 by utilizing cetyltrimethylammonium bromide (CTAB), a kind of C12TA.[75] The authors speculated that CTAB layers were responsible for the lattice alignment between ZIF-8 and Pd nanocube.

For the above surfactant-stabilized MNPs confined into ZIF matrix, it is difficult to remove the surfactant layers between ZIFs and MNPs completely. Thus, it may hinder the reactants from approaching active metal in catalysis. Considering this, some removable materials (e.g., Cu2O, SiO2, etc.) are selected as metal-stabilizing reagents for coating metal nanocrystals before encapsulation.[76,77] Tsung’s group reported an encapsulation strategy based on removable Cu2O for preparing nanocrystal confined into polycrystalline ZIF-8.[76] Pre-synthesized metal nanocrystal was coated with Cu2O, and then a layer of polycrystalline ZIF-8 was coated on Cu2O surface. Notably, cuprous oxide interlayer could be etched off simultaneously by the protons generated during the formation of ZIF-8. In recent years, many novel metal-stabilizing reagents are also emerging. Divesh N. Srivastava’s group developed citrate-stabilized Au nanoparticles, which were then encapsulated into the ZIF-8 frameworks along with glucose oxidase (GOx) to obtain GOx@ZIF-8(AuNPs) composites.[78] Shi and co-workers successfully encapsulated Au125 clusters protected by surface thiolate ligand glutathione into ZIF-8 frameworks (Figure 4A).[64] In addition, as shown in Figure 5B, Wang et al. innovatively utilized 2-methyl imidazole (organic ligand of ZIF-8) to stabilize foreign Pt nanoparticles. Then the introduction of Zn2+ into the above system could effectively encapsulate Pt nanoparticles with a diameter of 2–3 nm during ZIF-8 crystallization.[79] As written here, two main synthetic strategies of ZIF-confined metal nanoparticle catalysts have been described in detail.

FIGURE 5 Encapsulation strategy during ZIF crystallization. A, Formation and characterization of Pd nanocubes engaged in single-crystalline ZIF-8: (i) scanning electron microscopy (SEM) and (ii) TEM images of core–shell Pd@ZIF-8 nanocomposites. Reproduced with permission.[75] Copyright 2014, American Chemical Society. B, Synthesis and characterization of highly dispersed Pt NPs within ZIF-8: (i) HRTEM and (ii) the dark-field scanning transmission electron microscopy (DF-STEM) images of Pt@ZIF-8 showing homogenously dispersed Pt nanoparticles (bright spots in DF-STEM image). Reproduced with permission.[79] Copyright 2013, Royal Society of Chemistry.
3.2 Synthesis of ZIF-confined atomically dispersed metal catalysts

In addition to ZIF-confined MNPs, it is worth mentioning that atomically dispersed metal catalysts have been constructed within ZIF frameworks in recent years.\cite{28,80,81} These metal sites confined into ZIFs have the advantage of utilizing molecular-scale pores to achieve size-selective catalysis.\cite{28} Herein, based on the available but not many literature, two main synthetic strategies are summarized, that is, in situ transformation of metal nodes and encapsulation strategy during ZIF crystallization.

3.2.1 In situ transformation of metal nodes

In ZIFs, intrinsic metal nodes (Zn$^{2+}$ and Co$^{2+}$) are fully tetrahedral coordinated with imidazolate linkers thereby showing poor catalytic activity. But these single-atomically dispersed metal nodes are desirable for fabricating isolated metal sites with catalytic activity (unsaturated coordination and redox activity) via in situ transformation process. In this process, changing coordination number and coordination atom species of metal nodes by chemical approaches are key. Such in-situ transformation has been realized by the plasma treatment which is effective to etch nanomaterials. In 2017, atomically dispersed CoO$_x$ species in ZIF-67 (CoO$_x$-ZIF) were prepared via O$_2$ plasma treatment by Wang’s group.\cite{80} As shown in Figure 6A, O$_2$ plasma treatment could in situ transform Co nodes of ZIF-67 into CoO$_x$ species by breaking intrinsic Co-N bonds of ZIF-67 to form Co-O bonds. These atomic-scale CoO$_x$ species showed excellent redox activity during catalysis. Furthermore, the same group also fabricated coordinately unsaturated metal sites in ZIF-67 by using dielectric barrier discharge (DBD) plasma etching to partially remove imidazolate ligands attached to Co nodes (Figure 6B).\cite{81} Co-N$_4$ species were partially converted into Co-N$_x$ (x < 4) species that resulted from the removal of partial imidazolate ligands during plasma treatment. Meanwhile, these Co sites were found to be still atomic dispersion and possess excellent electrocatalytic performance. In conclusion, in situ transformation of metal nodes was a facile strategy to fabricate ADMSs with unsaturated coordination and redox activity within ZIF frameworks.
3.2.2 Encapsulation strategy during ZIF crystallization

In 2019, Li and co-workers prepared Ru3 triatomic clusters and Ru single atoms anchored on ZIF-8 (Ru3@ZIF-8 and Ru@ZIF-8 catalysts) via encapsulation and reduction processes. As shown in Figure 6C, the precursor triruthenium dodecacarbonyl (Ru3(CO)12) and ruthenium 2,4-pentanedionate (Ru(acac)3) was in situ encapsulated into ZIF-8 cages during ZIF-8 crystallization. Then atomically dispersed Ru3 clusters and Ru single atoms were formed after thermal reduction treatment. The authors speculated that carbon atoms of imidazolate linkers might stabilize these atomically dispersed metal species. In summary, ZIFs are promising porous supporters to stabilize ADMSs for catalysis directly.

4 SYNTHESIS OF ZIF-DERIVED CARBON-SUPPORTED METAL CATALYSTS

4.1 Synthesis of ZIF-derived carbon-supported metal nanoparticle catalysts

ZIF-derived carbon-supported MNPs are another promising class of heterogeneous metal catalysts. During high-temperature carbonization, pore structures of ZIFs can effectively prevent the growth of metal species, thus forming small MNPs embedded on nitrogen-doped carbon. And catalytically active MNPs embedded on nitrogen-doped carbon are not easy to aggregate in catalysis because of carbon protection and metal-nitrogen interaction. In earlier years, the fabrication strategy of ZIF-derived carbon-supported MNPs was mainly direct pyrolysis of ZIFs with certain metal nodes (e.g., Co-containing ZIF-67) to obtain corresponding MNPs. In order to introduce foreign metal species, researchers have gradually developed a series of synthetic strategies. Herein, these synthetic strategies of ZIF-derived carbon-supported metal nanoparticle catalysts are classified and reviewed as follows.

4.1.1 Direct pyrolysis of pristine ZIFs, bimetallic ZIFs, core-shell structured ZIFs and ZIF nanoarrays

Direct pyrolysis of pristine ZIFs

Cobalt imidazolate frameworks, in which each Co2+ is coordinated with four nitrogen atoms of 3,5-imidazolate linkers, were selected as precursors for preparing carbon-supported cobalt catalysts in 2011. When the pyrolysis temperature exceeded 500 °C, finely dispersed Co crystallites were formed within carbon skeleton. In 2012, the same group utilized iron imidazolate framework (FeIM), in which Fe2+ ions were coordinated either tetrahedrally or octahedrally through imidazolate linkers, as precursors for preparing carbon-supported iron catalysts. Furthermore, Zou’ group prepared Co nanoparticles (about 10 nm) that were uniformly dispersed in ZIF-67-derived carbon polyhedrons. Other carbon-supported Co nanoparticle catalysts have also been fabricated via pyrolysis of ZIFs.

Direct pyrolysis of bimetallic ZIFs

In 2015, Jiang and co-workers first selected bimetallic ZIFs as precursors to prepared carbon-supported cobalt catalysts. Almost simultaneously, based on bimetallic ZnxCo1-x(MeIM)2 (MeIM was 2-methylimidazole, x referred to the molar ratio of Zn), You et al. independently prepared a series of cobalt-nitrogen-carbon (Co-N-C) electrocatalysts. As shown in Figure 7A, ZnxCo1-x(MeIM)2 was synthesized via self-assembly of Zn2+ and Co2+ with 2-methylimidazole and then underwent pyrolysis at 900 °C to produce Co-N-C-x samples (x stands for the molar ratio of Zn in corresponding precursor bimetallic ZIFs). Notably, with the increase of molar ratio of Zn (i.e., x increasing) in the bimetallic Zn0.8Co0.2(MeIM)2, the size of Co nanoparticles in corresponding Co-N-C (bright white spots in scanning transmission electron microscopy (STEM) images) decreased significantly and Co nanoparticles were not visible in Co-N-C-0.8 due to low Co content. In these samples, the Co-N-C-0.8 derived from Zn0.8Co0.2(MeIM)2 showed optimized catalytic performance, in which mean diameter of Co nanoparticles was about 9.5 nm. The authors speculated that uniformly distributed Zn species could spatially isolate cobalt nodes and suppress sintering of cobalt species during pyrolysis, thus forming small-sized Co nanoparticles. In 2017, Long et al. designed a novel bimetallic Co-Ni-ZIF for direct pyrolysis to obtain CoNi alloy nanoparticles with mean size of 19.40 nm.

Direct pyrolysis of core-shell structured ZIFs

In 2015, a novel core-shell structured ZIF crystal (ZIF-8@ZIF-67), which consisted of ZIF-8 as the core and ZIF-67 as the shell, was well designed and synthesized via a seed-mediated growth method based on ZIF-8 and ZIF-67. Such core-shell structured ZIF-8@ZIF-67 crystals were converted into nitrogen-doped carbon/graphitic carbon (NC@GC) solid particles containing Co nanoparticles under pyrolysis. As shown in Figure 7B, ZIF-8 seeds were formed by self-assembly of Zn2+ with 2-methylimidazole. Then, seed-mediated growth was implemented to obtain core-shell structured ZIF-8@ZIF-67 crystals by adding
Co$_2^{+}$ and 2-methylimidazole. In this process, Co$_2^{+}$ and 2-methylimidazole could epitaxially grow into ZIF-67 shells on the surface of ZIF-8 crystals. Finally, the ZIF-8 cores were converted into nitrogen-doped carbon cores, while the ZIF-67 shells were converted into graphitic carbon shells containing Co nanoparticles during pyrolysis. After acid leaching with HF solutions to remove the residual Zn and Co species, the remaining Co nanoparticles with size of 7–8 nm were mostly located in the graphitic carbon shell regions and well protected by the graphitic carbon. This synthetic route not only proposes an elaborate core-shell structured ZIF-8@ZIF-67 crystal but also reasonably integrates nitrogen-doped carbon (NC) and graphitic carbon (GC) into one hybrid carbon particle for the first time. And Co nanoparticles are generally well dispersed in graphite carbon shell regions of NC@GC and therefore more accessible to reactants in catalysis.

Since then, such NC@GC hybrid materials have been frequently reported in which Co nanoparticles are well distributed into graphite carbon shells.[85–87] For example, Qiu and co-workers prepared double-shelled hybrid nanocages (DSNCs) with outer shells of Co-N-doped graphitic carbon (Co-NGC) and inner shells of nitrogen-doped carbon (NC) (denoted as NC@Co-NGC DSNCs) based on core-shell structured ZIF-8@ZIF-67.[85] The core-shell structured ZIF-8@ZIF-67 crystals were synthesized by a similar seed-mediated growth method followed by carbonization and acid leaching to obtain NC@Co-NGC DSNCs (Figure 7C). In contrast to other reported solid particle forms, a well-defined double-shelled hollow...
nanocage was finally fabricated. In such closely packed double-shelled structures, loose Co-NGC outer shells had a distorted surface anchored with many carbon nanotubes (CNTs) and Co nanoparticles with the size of several nanometers were enclosed by well-developed graphitic carbon; whereas dense NC inner shells were derived from ZIF-8 and consisted mainly of nitrogen-doped amorphous carbon. It was worth noting that Co nanoparticles were responsible for forming graphitic carbon and carbon nanotubes.

**Direct pyrolysis of ZIF nanoarrays**

With the development of the architecture design of ZIFs, a variety of novel materials, including ZIF nanoarrays, have been constructed and applied to electrocatalytic energy conversion. In some cases, 2D Co-containing ZIF arrays are well aligned on substrates (e.g., carbon cloth and Ni foam) through a solution growth method.[89,90] ZIF arrays can be transformed into nanoarray materials with carbon, metal and metal oxides as the main active species by high-temperature pyrolysis and facile post-synthesis treatment.[91–93] As shown in Figure 8A, Wang and co-workers successfully prepared hollow Co$_3$O$_4$ nanosphere embedded into carbon arrays through the carbonization and oxidation of Co-containing ZIF arrays grown on carbon cloth.[94] Their research suggested that carbon nanoarrays and hollow Co$_3$O$_4$ nanospheres exhibited promising catalytic performance toward both OER and ORR. Furthermore, Co/Co$_2$N$_x$ nanoparticles embedded into carbon arrays were also synthesized by the carbonization and nitridation of ZIF arrays supported on carbon cloth.[95]

In addition to carbon cloth, Ni foam and nanofibers are also good scaffolds for ZIF nanoarrays. For example, 2-methylimidazole (2-MIM) and Co(NO$_3$)$_2$·6H$_2$O were used to form Co-containing ZIF nanowire arrays on the surface of Ni foam. After thermal annealing in air, ZIF arrays were converted into Co$_3$O$_4$ nanowire arrays.[90] Besides, Guo et al. delicately prepared leaf-like Co-ZIF arrays anchored on the surface of nanofibers via impregnation procedure. Then, Co$_3$O$_{4-x}$ hollow nanoparticles with oxygen vacancies (Co$_3$O$_{4-x}$ HoNPs) supported on porous N-doped carbon were synthesized through the carbonization and oxidation of the above materials (Figure 8B). Notably, Kirkendall effect during oxidation process may play a crucial role in introducing oxygen vacancies into Co$_3$O$_4$ particles.[96]

### 4.1.2 Impregnation strategy

Although direct pyrolysis can effectively convert metal nodes into MNPs, this method cannot be used to synthesize various MNPs (e.g., noble metal nanoparticles) because considerable metal ions cannot serve as metal nodes of ZIFs. However, impregnation, which is good at introducing foreign metal precursors into porous materials, has great application space to prepare ZIF-derived carbon-supported MNPs. Foreign metal precursors can be introduced into ZIF pore structures by impregnation process and then reduced to MNPs by surrounding carbon during pyrolysis. In 2019, Chen and co-workers prepared Co nanoparticles confined in carbon cages through a two-step synthesis method, which consisted of double-solvent
impregnation and pyrolysis under Ar atmosphere. These Co nanoparticles with mean diameter of 6.2 nm were highly dispersed into nitrogen-doped carbon matrix. In addition to impregnating metal precursors into ZIFs, some scientists have chosen to directly impregnate metal precursors into ZIF-derived carbon. For example, Hu et al. successfully prepared atomically ordered intermetallic PdZn nanoparticles in calcinated ZIF-8 (ZIF-8C) via co-reduction process. ZIF-8C was first synthesized by calcination of ZIF-8 at 650 °C. Na2PdCl4 was then sufficiently impregnated to ZIF-8C in solution under vigorous stirring. Ultimately, adsorbed Pd2+ and near Zn sites were reduced together to intermetallic PdZn compounds in H2 gas at 400 °C, that is, co-reduction process. It is noteworthy that uniform pores of ZIF-8C exhibited confinement effect for ultrasmall PdZn nanoparticles in preparation. Hence, as shown in Figure 7D, PdZn nanoparticles with average sizes of 2.7, 1.8 and 1.2 nm showed excellent size uniformity.

4.1.3 Some other synthetic strategies

Galvanic replacement reaction
Recently, specific core-shell structured MNPs, which consist of non-noble metal as the cores and noble metal as the shells, have been successfully fabricated in ZIF-67-derived carbon via galvanic replacement reaction. Li and co-workers first prepared Co nanoparticles embedded into porous carbon (Co/NC) by carbonizing newly prepared ZIF-67. Subsequently, Co/NC was exposed to Pd(NO3)2 in solution, in which a spontaneous galvanic replacement reaction occurred between Pd2+ and Co0 (Co0 + Pd2+ → Co2+ + Pd0). Due to Pd2+ was reduced into Pd0 and then deposited on Co nanoparticle surface, desired Co@Pd core-shell nanoparticles with a mean diameter of 9.4 nm were fabricated.

Microwave-assisted method
Microwave-assisted method successfully introduced Ni3Fe alloy nanoparticles into cobalt-nitrogen-carbon materials (Co-N-C) via a rapid microwave-assisted method. In the synthetic route, bimetallic Co-doped ZIF-8, formed by self-assembly of Co2+ and Zn2+ with 2-methylimidazole, was first carbonized into Co-N-C materials at high temperature. Then Ni/Fe precursors (iron(III) 2,4-pentanedionate and nickel(II) 2,4-pentanedionate) and Co-N-C were mixed and underwent microwave treatment to obtain Ni3Fe alloy nanoparticles with the average size of 11.2 nm embedded into Co-N-C matrix. Interestingly, this microwave treatment realized preparation and uniform dispersion of nanoparticles in only 1 minute.

4.2 Synthesis of ZIF-derived carbon-supported atomically dispersed metal catalysts

Although showing high catalytic activity, scientists have gradually discovered that metal nanoparticles might not be the ideal catalyst mode. In metal nanoparticle catalysts, catalytic activity, and selectivity differences exist among surface metal atoms with different coordination environments, and unexposed internal atoms lead to low metal atom utilization efficiency. On contrast, atomically dispersed metal catalysts, such as single-atom catalysts, dual-atom catalysts, and triatomic metal cluster catalysts, possess distinctive coordination environment, and maximum atom utilization efficiency. Hence, atomically dispersed metal catalysts have risen up as research frontier of catalysis. Recently, ZIFs are widely selected as self-sacrificed precursors for the synthesis of atomically dispersed metal catalysts. In ZIFs, metal nodes are single-atomically dispersed, and metal precursors with suitable size can be spatially confined into cavities of ZIFs during one-to-one encapsulation. Nitrogen-doped carbon derived from ZIFs can provide abundant active nitrogen sites for anchoring metal atoms to avoid severe aggregation in synthetic and catalytic processes. According to these reported advances, synthetic strategies are classified, and detailed below.

4.2.1 Direct pyrolysis of bimetallic ZIFs and ZIF nanoarrays

Considering that metal nodes are atomically dispersed, direct pyrolysis of ZIFs has great potential for fabricating single-atom metal catalysts. However, numerous studies have demonstrated that direct pyrolysis of pristine ZIFs (such as ZIF-67) only produced MNPs because of drastic sintering of adjacent metal nodes. With the emergence and development of bimetallic ZIFs containing two kinds of metal nodes, this problem is gradually solved. In bimetallic ZIFs, target metal ions can partially replace original metal nodes to form bimetallic ZIFs. Since imidazolate linkers and original metal nodes can serve together as “fences”, target metal atoms are prevented from aggregating into MNPs during high-temperature pyrolysis. Eventually, these isolated target metal sites are stabilized by nitrogen of ZIF-derived carbon materials. Given the multitude of direct pyrolysis of bimetallic ZIFs published, the key to synthesizing isolated metal sites is to achieve highly homogeneous distribution of target metal nodes and original metal nodes within bimetallic ZIFs.
In 2016, Li’s group successfully prepared Co single atoms (Co SAs/N-C) by direct pyrolysis of bimetallic Zn/Co MOFs. As for the formation mechanism of Co single atoms at high temperature, the authors speculated that Zn nodes not only provided more active nitrogen sites because of zinc evaporation but also effectively varied the distance of adjacent Co atoms to avoid forming Co-Co bonds (Figure 9A). Isolated dispersion of cobalt sites and local atomic structure (Co-Nx architectures) were further revealed by XAFS involving extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) (Figure 9B). Notably, by increasing the pyrolysis temperature, the coordination environment of Co single atoms might transform Co-N4 (800 °C) to Co-N2 (900 °C). Since this successful synthesis of Co single atoms, direct pyrolysis of bimetallic ZIFs had been used to synthesize other single-atom catalysts (such as Ni, Fe). In 2017, the same group reported single-atom Ni catalyst by pyrolysis of bimetallic ZnNi-ZIF (Figure 9C). Zhang et al. developed chemical doping approach to synthesize single atomic iron catalysts (Figure 9D). In contrast to physical Fe ions adsorption, chemical doping approach meant that a small amount of Fe3+ mixed with Zn2+ was introduced into methanol solutions containing 2-methylimidazole. These Fe ions might bond with imidazolate ligands to form tetrahedral Fe-N4 during ZIF-8 crystallization. Eventually, single-atom Fe catalysts were obtained by direct pyrolysis of bimetallic Fe-doped ZIF-8.

In recent years, single-atom catalysts derived from bimetallic ZIF precursors have been continuously reported. In 2018, Wang et al. successfully controlled the coordination number over single Co sites derived from bimetallic Zn/Co ZIFs. By changing the pyrolysis temperature (800, 900, and 1000 °C), as shown in Figure 10A, single-atom Co catalysts with different nitrogen coordination numbers (Co-N4, Co-N3 and Co-N2) were prepared. In Figure 10B, the orderly decrease of Co-N peak intensity in EXAFS spectra and Co oxidation state in XPS spectra confirmed that atomic Co-Nx architectures changed with pyrolysis temperature. Furthermore, bimetallic Fe-doped ZIF-8 nanocrystals were loaded onto the surface of 2D graphene oxide and then pyrolyzed to...
2D porous Fe-N-doped graphene nanosheets with atomically dispersed Fe sites.\textsuperscript{[109]} They claimed that Fe-doped ZIF-8 nanocrystals were thermally molten onto graphene sheets to form single-atom Fe catalysts supported on 2D materials. Although direct pyrolysis of bimetallic ZIFs is facile, such synthetic strategy is limited to those target metal ions (Co\textsuperscript{2+}, Fe\textsuperscript{2+}, Fe\textsuperscript{3+}, and Ni\textsuperscript{2+}) that can serve as metal nodes of ZIFs and are similar to zinc ions in size and coordination.

Recently, ZIF nanoarrays have also been developed as suitable precursors for the preparation of single-atom catalysts. For example, Wang and co-workers successfully transformed ZIF arrays supported on carbon cloth into carbon flake arrays containing well-dispersed Co single atoms via a carbonization-acidification process.\textsuperscript{[111]} In the above catalysts, it is believed that abundant Co-N\textsubscript{x} sites and porous structures achieve high catalytic performance. Similarly, Ji et al. also developed single-atom catalysts (Co and Ni single atoms) via carbonization and acidification of ZIF arrays supported on electrospun nanofibers.\textsuperscript{[112]} The authors believed that this design strategy based on ZIF nanoarrays would provide ingenious ideas for constructing free-standing single-atom materials and binder-free catalytic electrodes.

### 4.2.2 Spatial confinement strategy

Metal precursors with suitable size can be uniformly encapsulated into regular pore structures of ZIFs. In subsequent pyrolysis, ADMSs resulting from precursor decomposition are anchored by active nitrogen sites.\textsuperscript{[113–116]} Recently, ZIF-8 with abundant molecular-scale cages is often adopted to encapsulate metal precursors. Suppose the size of metal precursors is between the pores (diameter of 3.4 Å) and cavities (diameter of 11.6 Å) of ZIF-8. In that case, one precursor molecule can be confined into one ZIF-8 cage and not migrate freely. The above idea was first applied to the preparation of isolated single iron atoms anchored on nitrogen-doped carbon (Fe-ISAs/CN) with iron loading up to 2.16 wt\% by Li and co-workers.\textsuperscript{[46]} As shown in Figure 11A, main synthetic route consisted of two steps: (1) the mononuclear precursor Fe(acac)\textsubscript{3} (diameter of 9.7 Å) was in situ encapsulated into the ZIF-8 cavities, and (2) above materials were placed into a tube furnace for pyrolysis to obtain single-atom Fe catalysts. Up to now, considerable research efforts have demonstrated that spatial confinement strategy consisting of encapsulation and pyrolysis is a universal scheme for fabricating single-atom catalysts with 3d, 4p, 4d, and 5d elements as metal centers. In 2019, Xiao et al. successfully prepared single-atom Ir catalysts based on spatial confinement of Ir(acac)\textsubscript{3}.\textsuperscript{[59]} In 2020, Li’s group synthesized single-atom Rh catalysts via the encapsulation and pyrolysis of Rh(acac)\textsubscript{3}.\textsuperscript{[58]} Almost simultaneously, they also recommended the use of acetylacetonate for synthesizing various single-atom catalysts (Ir, Pt, Pd, Ru, Mo, Ga, Cu, Ni and Mn).\textsuperscript{[49]}

Other mononuclear organometallic complexes with suitable size can also be employed for spatial confinement strategy. Ferrocene (Fc) (6.4 Å) could be selected as metal precursors to prepare single-atom iron catalysts via spatial confinement strategy.\textsuperscript{[113]} Furthermore, Sun’s group
innovatively synthesized single-atom Fe-Nₓ-C catalysts by incorporating Fe-phen (phen = 1,10-phenanthroline) complexes into cavities of ZIF-8 followed by pyrolysis. And Wang et al. deliberately introduced iron (II) phthalocyanine (FePc) with the size of 14.6 Å, which is slightly larger than cavities (11.6 Å) of ZIF-8, into the synthetic solution of ZIF-8 to form FePc@ZIF-8 nanocomposites. Then, single-atom iron catalysts containing edge-hosted Fe-N₄ sites and hierarchical micro-mesoporous structures were obtained by subsequent pyrolysis and acid leaching process. As shown in Figure 11B, structural evolution in the synthetic route is described as follows. First, FePc molecule with size of 14.6 Å burst ZIF-8 cage and broken the pore confinement effect of cavity during encapsulation. During pyrolysis, ZIF-8 was carbonized into carbon frameworks containing micropores and mesopores. Those FePc molecules trapped within broken cavities were reduced into edge-hosted Fe-N₄ sites, whereas excessive FePc multimolecular aggregates were decomposed into Fe₂O₃ nanoparticles and enlarged mesopores because of the Kirkendall effect. Finally, acid leaching resulted in the removal of Fe₂O₃ nanoparticles and formation of hierarchical micro-mesoporous carbon structures. Micro-mesoporous structures and edge-hosted Fe-N₄ sites facilitated mass diffusion and electron transport during catalysis.

Spatial confinement strategy can also be employed for fabricating dual-atom catalysts and triatomic cluster catalysts. In 2017, Li and co-workers successfully synthesized Ru₃ clusters supported on ZIF-derived nitrogen-doped carbon via spatial confinement strategy. They chose Ru₃(CO)₁₂ with molecular diameter of about 8.0 Å as metal precursors to be encapsulated into cavities of ZIF-8. In subsequent pyrolysis, Ru₃ clusters resulting from Ru₃(CO)₁₂ decomposition could be stabilized by nitrogen sites. In 2019, Ye et al. synthesized a series of atomically dispersed iron sites (Fe single atoms, Fe₂ clusters and Fe₃ clusters) based on the spatial confinement strategy. In this synthesis, Fe(acac)₂, Fe₂(CO)₉ and Fe₃(CO)₁₂ were selected as metal precursors for encapsulation and then pyrolyzed into corresponding atomically dispersed iron species. In summary, spatial confinement strategy based on ZIFs is a universal scheme for fabricating atomically dispersed metal catalysts.

4.2.3 Impregnation strategy

In recent years, investigators have attempted to impregnate a small number of metal precursors into preformed ZIFs, followed by thermal treatment to yield atomically dispersed metal catalysts. Nonetheless, due to the uncontrollability of impregnation process, some metal precursors are adsorbed on the outer surface of ZIF nanocrystals instead of entering ZIF pore structures. As a result, samples may contain unstable metal/metal oxide nanoparticles that need to be removed by acid leaching. Xing’s group prepare single-atom Cr (Cr/N/C) catalysts based on impregnation strategy. In their scheme (Figure 12A), metal precursor CrCl₃ was impregnated into pores/channels of ZIF-8 and then single-atom Cr catalysts were obtained by pyrolysis and diluted HCl solution leaching.
It is worth mentioning that the double-solvent method is another effective impregnation approach for introducing foreign species into interior of porous materials. In 2017, Li and co-workers successfully incorporated Ni precursors to ZIF-8 pores/cavities via double-solvent method. ZIF-8 crystals were dispersed in n-hexane under ultrasound and then Ni(NO$_3$)$_2$ aqueous solution was injected into the above solution slowly under ultrasound and mixed well by vigorous stirring. Due to the immiscibility of water and n-hexane, Ni(NO$_3$)$_2$ aqueous solution would form stable droplets in the n-hexane, which could go inside ZIF-8 pores/cavities by the capillary force. This double-solvent method greatly facilitated impregnation process and minimized deposition of Ni precursors on the outer surface of ZIF-8. In subsequent pyrolysis, Ni single atoms embedded into nitrogen-doped porous carbon (Ni SAs/N-C) were directly obtained without acid leaching (Figure 12B). The authors speculated that ionic exchange process existed in pyrolysis. At high temperature, Ni$^{2+}$ ions near Zn nodes would occupy the nitrogen sites generated by evaporation of Zn nodes and be further reduced to Ni single atoms. In 2020, Ma et al. designed a similar synthetic route to fabricate atomically dispersed copper catalysts. First, Cu(NO$_3$)$_2$ precursors were incorporated into pores/channels of ZIF-8 via a double-solvent method. In subsequent pyrolysis, similar ionic exchange determined the formation of atomically dispersed Cu sites, and different coordination structure of Cu sites (CuN$_3$ or CuN$_4$) was realized by changing pyrolysis temperature (900°C and 800°C) (Figure 12C). A similar impregnation strategy has also been used in synthesis of dual-atom catalysts. For example, Wang et al. constructed Fe-Co dual sites supported on nitrogen-doped carbon ((Fe,Co)/N-C) with the assistance of bimetallic Zn/Co ZIFs. As shown in Figure 12D, bimetallic ZIFs with uniformly distributed Zn and Co nodes were first synthesized. Then, Fe salts were sufficiently immobilized into ZIF pores via a double-solvent method. Finally, Fe-Co dual sites were obtained by high-temperature carbonization. In 2019, Ren et al. also obtained similar Ni-Fe dual sites embedded on nitrogen-doped carbon by an analogical synthetic route.

4.2.4 Thermal atomization and gas-migration strategies

MNPs loaded on nitrogen-doped carbon can be converted into metal single atoms, that is, thermal atomization
process. In 2018, Li’s group discovered the gradual transformation of noble Pd nanoparticles to Pd single atoms at high temperature.\cite{37} The authors conjectured that the atomization and sintering processes of Pd nanoparticles coexisted in thermal treatment. Interestingly, atomization would dominate the evolution of noble metal species at above 900 °C, leading to the transformation of Pd-NPs into Pd single atoms. DFT calculations revealed that the breaking of Pd-Pd bonds and formation of stable Pd-N₄ structure at high temperature were essential driving forces of atomization. In the same year, Wu and co-workers also reported that non-noble metal nickel nanoparticles supported on nitrogen-doped carbon could be converted into Ni single atoms at high temperature.\cite{38} Similarly, the competition between sintering and atomization of Ni nanoparticles was discovered through in situ TEM (Figure 13A). The size of nickel nanoparticles was first increased at low temperature (< 400 °C). However, as the temperature was further elevated, Ni nanoparticles are gradually atomized. The authors speculated that when nickel nanoparticles were exposed to nitrogen-rich defects at high temperature, strong coordination between nitrogen and metal would split Ni atoms from nickel nanoparticles and eventually result in atomization of nanoparticles.

In addition to thermal atomization, gas-migration is another novel strategy for the construction of ADMSs, which achieves the transformation of bulk metal/metal oxide into isolated metal sites. In 2018, Li’s group reported the fabrication of Cu single atoms supported on nitrogen-doped carbon via gas-migration strategy.\cite{121} In their synthetic scheme, Cu atoms on the surface of Cu foam would form volatile Cu(NH₃)ₓ species under ammonia atmosphere, thus continuously escaping from the surface of Cu foam. These Cu(NH₃)ₓ species were eventually trapped by defect sites of nitrogen-doped carbon, generating atomically dispersed Cu sites. In addition, the transformation of bulk Cu₂O to Cu single atoms was first achieved by Wu’s group.\cite{122} As shown in Figure 13B, nitrogen-doped carbon derived from ZIF-8 was selected as substrates to capture and reduce volatile Cu₂O species escaping from bulk Cu₂O surfaces. Finally, single-atom catalysts with isolated copper sites were successfully prepared. In conclusion, thermal atomization, and gas-migration strategies can effectively utilize cheap and easily obtainable bulk metal/metal oxides and MNPs to synthesize single-atom catalysts, which is of great scientific and practical significance.

5. SOME SELECTION QUESTIONS AROUND ZIF-BASED METAL CATALYSTS

In recent years, the development of ZIF-based metal catalysts has attracted extensive research interest in the field of catalysis. Numerous MNPs and ADMSs have been constructed into ZIFs and ZIF-derived carbon via a variety of advanced synthetic strategies. In order to design catalysts with desired catalytic properties, it is crucial to select scaffolds and synthetic strategies.
5.1 | The selection of scaffolds (ZIFs or ZIF-derived carbon)

Zeolite-like topologies and micropores of ZIFs enable efficient sieving of small molecules, improving the catalytic selectivity of ZIF-confined metal catalysts. In other words, ZIF frameworks exhibit size selectivity toward substrate molecules, and only substrates with smaller size than ZIF apertures can enter ZIF interior and react with active metal species. In 2019, Li et al. successfully prepared ZIF-8-confined single Ru atoms and triatomic Ru$_3$ clusters for size-selective catalysis.$^{[28]}$ In their study, because of aperture of 3.4 Å, ZIF-8 could act as “molecular sieve” for olefins to achieve the absolute regioselectivity of catalyzing terminal alkynes but not internal alkynes. However, there are also drawbacks when selecting ZIFs as supporters of active metal species. In some cases, water stability of ZIFs is unsatisfactory, and ZIF hydrolysis under hydrothermal conditions have been discovered.$^{[123,124]}$ Some other reports suggested that both the anions of the zinc salt used to synthesize ZIFs and the anions in water environment may influence water stability of ZIFs.$^{[125,126]}$ Moreover, compared with carbon materials, conductivity of most ZIFs is poor, which restricts further applications of ZIF-confined metal catalysts in electrocatalysis. ZIF-derived carbon is regarded as excellent electrocatalytic materials due to their good conductivity, high surface area, micro/mesoporous structures, and abundant element doping. Meanwhile, close coupling of carbon matrix with active metal species is also another advantage of such catalysts. But long-term electrocatalytic process often leads to the dissolution of carbon structures in alkaline/acidic media. In summary, the selection of scaffolds for supporting metal catalysts should depend on catalytic requirements, catalytic reaction conditions, and active metal species.

5.2 | The selection of synthetic strategies

In the past decades, a variety of synthetic strategies for constructing ZIF-based MNPs and ADMSs have been developed. To obtain high-performance ZIF-based catalytic materials, the selection of synthetic strategies is crucial. The selection basis of existing synthesis strategies is summarized in Table 1.

6 | SUMMARY AND OUTLOOK

Rational design of nanocatalysts is always the critical task of catalytic science. Rapidly developing nanoscience has driven structural design of catalysts into the nano-era, which now again leads catalytic science into the atomic age. As a class of crystalline porous materials, ZIFs have exhibited high surface area, good structural tailorability and high stability. In addition, after high-temperature pyrolysis, ZIFs can be upgraded to porous carbon materials with abundant micro/mesopores and active nitrogen species (graphitic nitrogen, pyridinic nitrogen, and pyrrolic nitrogen). So far, various metal nanoparticle catalysts and atomically dispersed metal catalysts (single-atom, dual-atom, and triatomic cluster catalysts) have been fabricated through advanced synthetic strategies based on ZIFs and have shown great potential in catalytic processes involved in chemical production and energy conversion reactions, such as oxygen reduction reaction (ORR), CO$_2$ reduction reaction (CO$_2$RR), hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). These catalytically active metal species are either confined within ZIF frameworks (ZIF-confined metal catalysts) or stabilized by ZIF-derived carbon materials (ZIF-derived carbon-supported metal catalysts). In this review, we integrated the main synthetic strategies and underlying structural advantages of the above two nanocatalysts, and we hope that this review report will be useful in the design of small-sized metal catalysts using ZIFs and their derivatives as platform. For successful construction of small-sized metal catalysts, the following factors need to be considered: (1) effective incorporation and uniform dispersion of suitable metal precursors into molecular-scale pores/cages of ZIFs; (2) in situ transformation of metal nodes into ultrasmall nanoparticles or even single-atom sites with catalytic activity via specific approaches, such as plasma etching and designing bimetallic ZIFs; (3) evenly distributed nitrogen sites in ZIF-derived carbon for anchoring catalytically active metal species, especially to ADMSs. These viewpoints are conducive to rational design and structural regulation of metal catalysts.

Catalytic applications of ZIF-based MNPs and ADMSs are also fascinating and promising. ZIF-confined MNPs are usually used to catalyze organic reactions, such as hydrogenation of olefins. ZIF-confined ADMSs are applied to catalyze OER. On the other hand, excellent ORR activities of ZIF-derived carbon-supported metal catalysts have been confirmed. Remarkably, atomically dispersed M-N$_x$ sites (M = Fe, Co, Cu, Mn, or Ir) supported on ZIF-derived carbon have exhibited ultrahigh ORR activity, especially Fe-N-C sites, which are promising to replace platinum group metal (PGM) catalysts. Moreover, atomically dispersed Ni-N-C sites are efficient for electroreduction of CO$_2$. Inspired by the above high catalytic activities, the structural design of ZIF-based metal catalysts is also rapidly developing.

However, there are still deficiencies in structural regulation of metal catalysts, especially atomically dispersed metal catalysts. For instance, ZIF-derived nitrogen-doped
| Scaffold          | Metal specie | Synthetic strategy | Synthetic method                  | Advantage and selection basis                  |
|------------------|--------------|--------------------|-----------------------------------|------------------------------------------------|
| ZIFs             | MNPs         | Postsynthesis      | Impregnation                       | Easy operation                                  |
|                  |              | Encapsulation      | Chemical vapor deposition          | Uniform particle size                           |
|                  |              |                    | Solid grinding                     | Easy operation Uniform particle size            |
|                  |              |                    | Encapsulation /                   | Well-designed morphology and size of MNPs       |
|                  |              |                    | ADMSs / In situ transformation of metal nodes | Time-saving plasma etching                     |
| ZIF-derived      | MNPs         | Direct pyrolysis of ZIFs | Direct pyrolysis of pristine ZIFs  | High-dispersed metal sites                      |
| carbon           |              |                    |                                                                                   |
|                  |              |                    | Direct pyrolysis of bimetallic ZIFs | Controllable size of MNPs                       |
|                  |              |                    | Direct pyrolysis of core-shell structured ZIFs | Controllable heteroatom doping                   |
|                  |              |                    | Direct pyrolysis of ZIF nanoarrays | Hierarchically porous carbon structures          |
|                  |              | Impregnation        | /                                  | Free-standing and binder-free nanomaterials     |
|                  |              | Galvanic replacement reaction | /                                  | Easy operation                                  |
|                  |              | Microwave-assisted method | /                                  | Bimetallic core-shell nanoparticles              |
|                  |              | Direct pyrolysis of bimetallic ZIFs and ZIF nanoarrays | /                                  | Time-saving operation                           |
|                  |              | Spatial confinement | /                                  | Conventional metal sources Easy operation       |
|                  |              | Impregnation        | /                                  | High-dispersed atomic metal sites               |
|                  |              | Thermal atomization and gas-migration Strategies | /                                  | Easy operation                                  |
|                  | ADMSs        | Direct pyrolysis of bimetallic ZIFs | /                                  | Conversion from MNPs to ADMSs                   |

Carbon can provide uniform N/C coordination structures but cannot create various local coordination environments containing other heteroatoms (such as S, P, B, and O) for atomic metal sites. The introduction of foreign heteroatom sources is promising for modulating local coordination environment. For example, Li et al. reported the successful construction of atomic Co-P$_3$N$_3$ structures based on in situ phosphatizing of triphenylphosphine encapsulated into ZIFs.[127] Meanwhile, it remains challenging to promote the metal atom loading for ZIF-derived carbon-supported single-atom catalysts. More novel synthetic strategies and understanding of the formation process of metal single atoms in ZIF-derived carbon will be beneficial to boost the metal atom loading. And more approaches are also urgently desirable to improve the stability of ZIF-based metal catalysts under catalytic reaction conditions. In addition, Experimental and theoretical studies related to the catalytic process of atomically dispersed metal catalysts are still insufficient. With the development of nanotechnology, in situ measurements will help to further reveal catalytic mechanism and “structure-catalytic properties” correlations, such as in situ electron microscopic observation. We believe that these issues can be solved with the advancement of nanoscience, and structural design of metal catalysts based on ZIFs will surely have a bright future.

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**CONFLICT OF INTEREST**

The authors declare no conflicts of interests.

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