Review
Recent Advances in Carbon-Based Iron Catalysts for Organic Synthesis

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Abstract: Carbon-based iron catalysts combining the advantages of iron and carbon material are efficient and sustainable catalysts for green organic synthesis. The present review summarizes the recent examples of carbon-based iron catalysts for organic reactions, including reduction, oxidation, tandem and other reactions. In addition, the introduction strategies of iron into carbon materials and the structure and activity relationship (SAR) between these catalysts and organic reactions are also highlighted. Moreover, the challenges and opportunities of organic synthesis over carbon-based iron catalysts have also been addressed. This review will stimulate more systematic and in-depth investigations on carbon-based iron catalysts for exploring sustainable organic chemistry.

Keywords: carbon material; iron; heterogeneous catalysis; organic synthesis; green chemistry

1. Introduction

Organic synthesis has made great contributions to the progress of human society, but has also caused serious environmental pollution [1,2], so there is an urgent demand to introduce green chemistry into this area. One practical tool is the exploration of efficient and selective catalysts for organic synthesis, which can improve synthetic efficiency and reduce production costs and wastes, thereby minimizing the impact on the environment [3,4].

Iron, as the most productive and cheapest metal [5–7], is widely available, biocompatible and non-contaminant. The valence state of iron ranges from $-2$ to $+5$, which equips it with flexible redox properties, Lewis acidity and coordination ability [8]. Furthermore, iron-based enzymes are involved in lots of vital and efficient transformations in vivo [9]. All the above mentioned features of iron render a wonderful candidate to replace noble metals, and stand out among other non-precious metals. Therefore, iron-based catalysts meet the requirement of “catalyst economy”, and the development of these catalysts for organic transformations is conductive to the sustainable development of this area [6]. Nevertheless, the high chemical activity of iron also leads to its poor stability, which limits its application possibilities in more catalytic processes [10,11]. Meanwhile, iron has lower electronegativity and proportion of d orbitals and electrons than noble metals (such as Pd, Ru and Au), so it has poor catalytic activity in hydrogenation and cross-coupling reactions [12,13].

To solve these issues, ligands or supports are required to stabilize or tune the performance of iron sites [14–17]. Considering that ligands are relatively expensive and non-recyclable, solid supports are undoubtedly more in line with the requirements of green chemistry. Among various supports, carbon materials, with advantages of good biocompatibility, unique microstructure, high specific surface area and excellent physical and chemical properties, are considered excellent supports for iron-based heterogeneous catalysts [18–25]. Therefore, carbon-supported iron materials combining the advantages of iron and carbon materials are an efficient and sustainable catalyst for organic synthesis. In addition, N-doped carbon anchored iron-single-atom catalysts have similar FeN₄...
active sites with natural iron-based enzymes in terms of electronic, geometric and chemical structures [26,27].

Although there are several excellent reviews concerning the organic reactions over heterogenous and homogenous iron-based catalysts [4–8,28–37], no attempt focuses on the carbon-based iron catalysts for organic synthesis. In recent years, there have been dozens of organic transformations catalyzed by carbon-based iron materials, including oxidation, reduction, tandem and other reactions. Taking into account the advantages and development trends of nanocarbon-based iron catalysts for organic synthesis, the review on this kind of heterogenous catalysts for organic reactions is of great importance and appeal.

In this review, we thus focus on the recent progress on nanocarbon-based iron catalyzed organic transformations, which is categorized by the reaction types. The introduction strategies of iron into carbon materials and the structure and activity relationship (SAR) are also highlighted in this review. In addition, the challenges and opportunities of organic synthesis over nanocarbon-based iron catalysts have also been addressed.

2. General Consideration
2.1. The Introduction Strategies of Iron into Carbon Materials

The catalytic activity of carbon-based iron materials is closely related to their structures, which are controlled by their synthetic strategies. Because numerous reviews on carbon-based metal materials have systematically summarized the controlled fabrication of these materials [38–40], this review mainly focuses on the introduction methods of iron into carbon materials. There are three main steps for the preparation of these catalysts: precursor synthesis, pyrolysis and post-modification (Figure 1). In the precursor synthesis step, iron can be introduced by mechanical mixing, self-assembly and impregnation methods [41–43]. Chemical vapor deposition (CVD) can be applied for iron doping during the pyrolysis process [44–46]. Impregnation is also an efficient approach for anchoring iron to carbon material in the post-modification step.

Figure 1. Schematic illustration for the introduction of iron species into carbon supports.

2.1.1. Mechanical Mixing Strategy

Mechanical mixing refers to the direct mixing of iron sources and precursor compounds, without special treatment and requirements on the structure of the precursors. Although this method is easy to be operated, it results in the non-uniformity of carbon particle size and iron distribution [47]. Ball milling has been applied for more even mixing. In 2015, Deng et al. prepared FeN₄/GN with highly dispersed FeN₄ center by ball milling the mixture of iron phthalocyanine and graphene nanosheets (GNs) [48].
2.1.2. Impregnation Strategy

The impregnation strategy is to impregnate the solution of iron source with carbon materials or carbon precursors, with the removal of residual solvent after impregnation equilibration then leading to the introduction of iron species into carbon materials or carbon precursors [49]. In general, the impregnation method has better mixing efficiency than mechanical mixing, resulting in a more uniform Fe doping. However, the impregnation method still cannot effectively solve the problem on the inhomogeneity of carbon particle size and iron distribution. For example, ethyl cellulose was dissolved in ethanol and mixed with the aqueous solution of Fe(NO$_3$)$_3$·9H$_2$O, and then melamine and zinc nitrate were added as nitrogen source and pore former, respectively (Figure 2a) [50]. However, the size and distribution of carbon and iron particles in Fe@CN-Zn are not uniform, which can be observed from the results of TEM (Figure 2b) and SEM (Figure 2c).

![Figure 2. (a) Schematic illustration of the synthesis of Fe@CN-Zn. (b) TEM and (c) SEM images of Fe@CN-Zn. Reprinted with permission from Ref. [50]. Copyright 2021, Elsevier.](image)

2.1.3. Self-Assembly Strategy

The introduction of iron can also be achieved through the self-assembly of iron salts with certain organic ligands to form ordered 3D porous metal-organic frameworks (MOFs), which can be divided into two types: Bimetallic MOFs and Fe-based MOFs. Compared to other methods, nanocarbon-based iron catalysts prepared from self-assembly precursors have advantages of ordered porous structure, more uniform carbon size and iron distribution [51–53]. However, this approach has special requirements for organic ligands, which should be able to coordinate with iron ions to form MOFs.

As a bimetallic MOF strategy example, Fe-ZIF (ZIF represents zeolitic imidazolate framework) was prepared via the self-assembly of iron salts and zinc nitrates with 2-methylimidazoles (Figure 3a) [43]. An N-doped carbon-based iron catalyst was synthesized by the pyrolysis of Fe-ZIF. As a representative example of Fe-based MOF strategy, MIL-101(Fe) was prepared by self-assembly of 1,4-terephthalic acid with iron nitrate hexahydrate, which was grinded with melamine and then calcinated to obtain Fe/Fe$_2$O$_3$@N$_x$PC-T-x catalyst (n represents the ratio of MIL-101 (Fe) and melamine, T represents calcination temperature and x represents calcination pyrolysis time) (Figure 3b) [54].
2.1. Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD) refers to a vapor phase self-assembly carbonization process at high temperatures, which can effectively control the chemical composition, morphology, crystal structure and grain size of the membrane layer by adjusting the deposition parameters [55]. This method can make iron species in full contact with the carbon materials during the carbonization process, constructing a unique active iron center, and finally obtaining a catalyst for carbon-loaded iron with excellent catalytic activity. In 2021, Jia et al. prepared a Fe-N-C catalyst containing dense FeN sites by flowing iron vapor through the Zn-N-C substrate at 750 °C (Figure 4) [56].

Figure 3. (a) The preparation of Fe₅₆₅₃/Fe₂O₃NPC from bimetallic MOF strategy. Reprinted with permission from Ref. [43]. Copyright 2020, American Chemical Society. (b) The preparation of Fe/Fe₂O₃@NPC-700-x from Fe-based MOF strategy. Reprinted with permission from Ref. [54]. Copyright 2019, Wiley.

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Figure 4. Preparation of FeNC-CVD-750 via CVD strategy. Reprinted with permission from Ref. [56]. Copyright 2021, Springer Nature.

2.2. The Structure and Activity Relationship (SAR)

2.2.1. Nature Properties of the Carbon Materials

In comparison of metal oxide supports, carbon materials have unique porous structure, and are easier to be doped with heteroatoms, which can adjust their Lewis acid-base sites and defect the degree and electronic state of Fe sites, facilitating the formation of stable and active iron catalytic sites. Therefore, iron-doped carbon materials exhibit superior performance than metal oxide-supported iron catalysts in various transformations. For example,
Beller’s group have prepared two carbon-supported iron catalysts: Fe-phenanthroline/C-800 [57] and Fe-L1@EGO-900 [41], which exhibit good catalytic activity for the reduction of nitroarenes and acceptorless dehydrogenation reactions, respectively. The two catalysts were prepared by calcinating the mixture of iron precursor, 1,10-phenanthroline ligand and carbon support. The difference is that carbon powder was used as carbon support in Fe-phenanthroline/C-800, while exfoliated graphene oxide (EGO) was applied as carbon support in Fe-L1@EGO-900. However, the catalytic efficiency of other heterogeneous iron catalysts is much lower, or even with no catalytic effect when the carbon material is replaced with other carriers, such as Al$_2$O$_3$, SiO$_2$, CeO$_2$ and TiO$_2$. Overall, the porous structure and defects of carbon supports are favorable for the interaction between substrates with active sites, as well as the exposure of active sites in the catalysts. The Lewis acid-base sites of carbon supports can improve the adsorption and activation of substrates.

2.2.2. Iron Sites in Carbon Materials

Generally, there are two types of iron sites in carbon materials: single atomic iron sites and iron nanoparticles (NPs) [58,59]. The identification of these two iron sites can be achieved by XRD, TEM, XAFS and HAADF-STEM [60–62]. Single atomic iron sites and iron nanoparticles (NPs) can usually play a synergistic catalytic role by exerting their respective catalytic advantages in different steps of one reaction [58,60,63]. Although some control experiments have been designed to verify the synergistic catalytic effect between these two sites, the research on this aspect is still in its infancy.

For example, Yang et al. designed a series of control experiment to confirm the synergistic catalysis on FeN$_x$ sites (single atomic Fe sites) and Fe NPs for the fabrication of quinolones and quinazolinones (Figure 5a) [58]. Because acid etching can remove Fe NPs selectively, while SCN$^-$ can specifically poison FeN$_x$ sites, the catalytic effects of FeN$_x$ and Fe NPs in the reaction can be clarified. In addition, the reaction principles of Fe(II)Pc and nano-Fe powder are similar to that of FeN$_x$ sites and Fe NPs, which are also applied to detect the role of FeN$_x$ and Fe NPs during the catalytic process. The coupling reaction of amine and aldehyde and the oxidative dehydrogenation of intermediate I are the two steps involved in the oxidative coupling reaction (Figure 5a). As shown in Figure 5a, FeN$_x$ sites are more favorable for the formation of intermediate I, while Fe NPs are more conducive to the further dehydrogenation of intermediates I to produce quinolones and quinazolinones. Thus, FeN$_x$ sites and Fe NPs play a synergistic catalytic role in this oxidative coupling reaction.

FeN$_x$ site has similar structure with active sites of natural iron-based enzymes, so it exhibits excellent redox performance under mild conditions. Meanwhile, the coordination environment of iron single-atom sites can also be regulated by manipulating the preparation parameters, such as heteroatom doping, which may further improve the catalytic performance of iron sites. For example, Li et al. prepared phosphorus-doped atomically dispersed catalyst Fe-P-C for the first time, and found that the resulting O$_2$–Fe-P$_4$ structure is reduced by hydrogen to generate a large number of Fe-P$_4$ sites, which is attributed to the excellent catalytic performance of the catalyst in the hydrogenation reaction (Figure 5b) [64]. However, the FeN$_4$ sites generated in Fe-N-C prepared by nitrogen atom doping are less active towards the same reaction.

In general, FeN$_x$ sites have higher atom utilization and catalytic efficiency than iron NPs, while Fe NPs in the catalysts do play a non-negligible catalytic role in many reactions. This is mainly because many organic reactions inherently involve multi-step steps that require the synergy of multiple active sites.
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Figure 5. (a) The control experiments on the synergistic catalysis between FeN\textsubscript{x} sites and Fe NPs. Reprinted with permission from Ref. [58]. Copyright 2019, Royal Society of Chemistry. (b) The synthetic route of Fe-P-C. Reprinted with permission from Ref. [64]. Copyright 2020, Springer Nature.

2.2.3. The Construction of SAR

The construction of SAR between carbon-based iron catalysts and organic reactions are mainly explored by control experiments, reaction kinetics studies and density functional theory (DFT). Control experiments are performed to determine possible reaction intermediates and reaction pathways by changing the reaction conditions or substrates appropriately, or by adding additives. As shown in Scheme 1, the role of Fe-Fe\textsubscript{3}C@NC-800 and H\textsubscript{2}O\textsubscript{2} in the reaction is investigated by control experiments. Based on the results of Scheme 1, it can be concluded that Fe-Fe\textsubscript{3}C@NC-800 is necessary for both the coupling and dehydrogenation process, while H\textsubscript{2}O\textsubscript{2} is favorable for the dehydrogenation process [58].

The main purpose of reaction kinetic studies is to determine the rate-determining step (RDS) of the reaction. RDS is the most critical step in the complex organic reactions, so determining RDS is beneficial to simplify the studies of the reaction mechanism. Kinetic isotope experiments (KIE) is a commonly used approach to determine RDS, in which the $k_{H}/k_{D}$ value can be an indicator for RDS [65]. The RDS can also be determined by detecting reaction orders, which reflects the effect of reactant concentration on the reaction rate. For example, our group determines the borrowing hydrogen N-alkylation reaction order of benzyl alcohol and benzylamine, and performs KIE to confirm the RDS (Figure 6) [66]. The reaction order of aniline in this reaction is negative, while that of benzyl alcohol is positive (Figure 6b,c), confirming the activation of benzyl alcohol may be involved in the RDS [67]. The parallel experiments are performed by using PhCH\textsubscript{2}OH and isotope-labeled PhCD\textsubscript{2}OH
to go through this reaction respectively, and the $k_H/k_D$ of this reaction is calculated to be 2.75 (Figure 6a), further indicating that the C-H activation of benzyl alcohol may be related to RDS.

### Scheme 1

The role of Fe-Fe$_3$C@NC-800 and H$_2$O$_2$ in mechanism exploration. Reprinted with permission from Ref. [58]. Copyright 2019, Royal Society of Chemistry.

### Figure 6

(a) The H/D kinetic isotope effect (KIE) experiment results. Plots of reaction orders of (b) aniline and (c) benzyl alcohol. (d) The energy barriers for Fe$_2$O$_3$, Fe$_3$-N$_4$O$_4$, Fe$_3$-N$_5$ and Fe$_3$-N$_4$S$_1$ sites. (e) The relationship between positive charge density of Fe sites and energy barriers. Reprinted with permission from Ref. [66]. Copyright 2021, Royal Society of Chemistry.
In addition, DFT calculations can further confirm the main catalytic active center in RDS by comparing the energy barriers, which can also provide useful information for the construction of SAR between carbon-based iron catalysts and organic reactions. For instance, to further identify the catalytically active center, the RDS energy barriers of different Fe sites can be calculated based on DFT [4,43,68–70]. The energy barriers of these four sites can be sorted as \( \text{Fe}_1\text{-N}_4\text{S}_1 \), \( \text{Fe}_1\text{-N}_5 \), \( \text{Fe}_1\text{-N}_4\text{O}_1 \), and \( \text{Fe}_2\text{O}_3 \), which are positively related to their positive charge density (Figure 6d,e). These results suggest that \( \text{Fe}_1\text{-N}_4\text{S}_1 \) and \( \text{Fe}_1\text{-N}_5 \) are more likely to be the main catalytically active sites for the RDS process [66].

Based on these results, a possible strategy for construction the structure-activity relationship is listed: (1) confirming the rate-determining steps of reactions and the main active sites of carbon-based iron catalysts by catalyst characterization data, control and kinetic experiments; and (2) establishing the relationship between the two based on reaction yields and structural information of the active sites, and confirming it by DFT calculations.

3. Oxidation Reactions

Compared to metal oxides, \( \text{O}_2 \) and metal-free peroxides are undoubtedly greener and safer oxidants, but their own oxidative capacity is relatively poor. Thus, further activation of these oxidants by certain catalysts is required. Iron features the ability to transfer electrons to \( \text{O}_2 \) and peroxides, thereby displaying excellent performance on many oxidation reactions. Furthermore, the porous carbon materials are favorable for the adsorption of \( \text{O}_2 \) and peroxides. Therefore, carbon-based iron catalysts show superior catalytic performance than noble metal-based catalysts in many oxidation reactions using \( \text{O}_2 \) or metal-free peroxides as oxidizing agents.

3.1. Selective Oxidation of Nitrogenous Compounds

In 2015, \( \text{FeO}_x \) NPs surrounded by nitrogen-doped-graphene shells that immobilized on carbon layers (\( \text{FeO}_x\text{NgGr-C} \)) were successfully prepared by simple pyrolysis process (Scheme 2a). This catalyst was applied in the oxidative dehydrogenation of \( \text{N} \)-heterocycles, which overcomes the poor functional-group tolerance and harsh condition requirements involved in the reported catalytic system (Scheme 2b) [17]. The high thermal stability and coordination ability of 1,10-phenanthroline promotes the formation of graphene shells around \( \text{FeO}_x \) NPs during the pyrolysis process, and the formed \( \text{N} \)-doped carbon layers with graphene-stacking defects lead to the exposure of active sites for \( \text{O}_2 \) absorption. In the same year, this group developed a similar catalyst (\( \text{Fe}_2\text{O}_3\text{NgGr-C} \)) to achieve the selective dehydrogenation of primary amines for the production of various aliphatic, aromatic and heterocyclic nitriles (Scheme 2c) [71]. It is worth noting that the use of excess aqueous ammonia can inhibit the formation of secondary imine, thereby improving the reaction selectivity. In addition, the unique carbon layer encapsulation structure makes the activity of \( \text{Fe}_2\text{O}_3\text{NgGr-C} \) not significantly decrease after 5 runs, exhibiting industrial application potential.
Scheme 2. (a) Schematic diagram for the preparation of FeO\(_x\)@NGr-C. (b) Oxidative dehydrogenation of tetrahydroquinolines catalyzed by FeO\(_x\)@NGr-C. Reprinted with permission from Ref. [17]. Copyright 2015, American Chemical Society. (c) Fe\(_2\)O\(_3\)/NGr@C catalyzed synthesis of nitriles. Reprinted with permission from Ref. [71]. Copyright 2015, Wiley.

3.2. Epoxidation of Olefines

The epoxidation of olefines provides a variety of important building blocks for the pharmaceutical and fine chemical industries [72]. In 2019, Kucernak et al. introduced a Fe-N/C catalyst by calcining the complex of polymerized 1,5-diaminonaphthalene and FeCl\(_2\) [73]. The FeN\(_x\) active sites in Fe-N/C are similar to that in Fe porphyrins, and thereby display excellent performance in the epoxidation of olefines, with O\(_2\) as the oxidant under mild conditions (Figure 7a). This is also the first example that such kind of catalysts are used for the aerobic epoxidation of olefins under mild conditions, which with high turnover frequency (2700 h\(^{-1}\)) and good recyclability can be reused 5 times.

Figure 7. (a) Epoxidation of olefines with Fe-N/C catalyst. Reprinted with permission from Ref. [73]. Copyright 2019, Elsevier. (b) Schematic diagram for the preparation of SAS-Fe.
An iron single-atom site catalyst (SAS-Fe) with 30 wt.% of Fe loading was fabricated by the reductive calcination of the complex formed by the coordination of dicyandiamide and Fe(NO$_3$)$_3$$\cdot$9H$_2$O (Figure 7b) [74], which overcomes the shortcomings of common SAS catalysts, such as low metal loading, and the aggregation and movement of single-atom-sites. Furthermore, DFT calculations were performed to study the catalytic mechanism of SAS-Fe (Figure 8). It was found that the difference in the energy barrier to generate epoxy styrene or benzaldehyde during the reaction can reach a maximum of $\Delta E_a = 0.83$ eV, revealing that SAS-Fe tends to promote the formation of epoxy styrene rather than phenylacetaldehyde. The selectivity of SAS-Fe to epoxy styrene can be as high as about 90%, and its activity remains unchanged after 5 cycles. Due to the high metal loading and scalable production, SAS-Fe does meet the requirement of industrial applications.

Figure 7. (a) Epoxidation of olefines with Fe-N/C catalyst. Reprinted with permission from Ref. [73]. Copyright 2019, Elsevier. (b) Schematic diagram for the preparation of SAS-Fe.

Figure 8. DFT calculations of styrene epoxidation over SAS-Fe (* represents the active sites). Reprinted with permission from Ref. [74]. Copyright 2020, Wiley.

3.3. Selective Oxidation of Hydrocarbons

In 2015, Deng et al. fabricated highly dispersed single FeN$_4$ centers by high-energy ball milling of the mixture of iron phthalocyanine (FePc) and graphene nanosheets (GNs) under controlled conditions. The obtained catalyst FeN$_4$/GN exhibits excellent activity for oxidizing benzene to form phenol at room temperature using H$_2$O$_2$ as oxidant [48]. The catalytic mechanism of FeN$_4$/GN is proposed based on the results of control experiments and DFT calculations, indicating that the formation of Fe=O moiety is a critical step to realize the transformation of benzene to phenol (Figure 9a).

Nanocarbon-supported iron catalysts were found to show “platinum-like” properties in catalytic reactions, while the specific active site on them still remains controversial. Along this line, Zhang et al. synthesized an atomically dispersed Fe-N-C catalyst for the selective oxidation of C-H bond in alkanes with high selectivity [60]. In order to investigate the main active site in Fe-N-C, a series of characterizations are performed, the results of which indicate that the atomic iron mainly exists in the form of FeN$_x$ (x = 4–6) (Figure 9b). Based on control experiments, FeN$_5$ shows the highest TOF compared to FeN$_4$ and FeN$_6$, although the content of FeN$_5$ is much lower. In addition, the content of FeN$_5$ sites decreases as the temperature raises from 700 °C to 800 °C, which in turn results in a significant loss of catalytic activity. It can be concluded that the content of FeN$_5$ depends on the calcination temperature, and can significantly affect the catalytic efficiency.
Control experiments, FeN₄, N-N, accelerated by the use of alcohol as an additional hydrogen source.

Figure 9. (a) The proposed catalytic mechanism for FeN₄/GN catalyzed transformation of benzene to phenol. (b) HAADF-STEM image of Fe-N-C and a turnover frequency (TOF) comparison of different iron sites on the Fe-N-C towards the oxidation of C-H bond. Reprinted with permission from Ref. [60]. Copyright 2017, American Chemical Society.

4. Reduction Reactions

In addition to oxidation reactions, nanocarbon-supported iron catalysts also show potential to catalyze reduction reactions [75,76]. Hydrodeoxygenation, hydrogenolysis and hydrogenation are three main kinds of catalytic reduction reaction over iron-doped carbon materials.

4.1. Hydrodeoxygenation

In 2017, Fu et al. described an effective iron catalyst (Fe-L1/C-800) by simultaneous calcination of 1,10-phenanthroline (L1) as the nitrogen precursor and activated carbon as the carrier at 800 °C, which could selectively realize the hydrodeoxygenation of HMF (5-hydroxymethylfurfural) to DMF (N,N-dimethylformamide), with a selectivity of 86.2% [77]. The hydrogenation of aldehyde group in HMF is found to be the rate-determining step, which can be accelerated by the use of alcohol as an additional hydrogen source. Moreover, this catalyst maintains excellent stability and high selectivity in both batch and continuous flow fixed-bed reactors.

The selective hydrodeoxygenation (HDO) of carboxylic acids to alkanes is of great importance for the production of biofuel from biomass [78]. Therefore, a N-doped carbon-alumina hybrid supported iron (Fe-N-C@Al₂O₃) catalyst was prepared by calcining the mixture of Fe(acac)₃, melamine and Al₂O₃ at 900 °C [79]. Surprisingly, the Fe-NC@Al₂O₃ catalyzed HDO of carboxylic acids displays excellent chemo-selectivity, even in the presence of an aromatic ring that is generally easier to be hydrogenated than carboxylic acid (Figure 10), which is ascribed to the formation of the Fe₃ active phase and N-doped carbon-alumina hybrid. Moreover, the formation of both nitrogen-doped carbo-alumina hybrid and iron loading effect the Lewis basicity of Fe-N-C@Al₂O₃ to adsorb substrates.
exhibits excellent chemical selectivity towards the hydrogenation of nitro compounds, and
society.
Figure 11. Schematic diagram of Fe-phen/C preparation and its catalyzed reduction reaction of
it does not inhibit the FeN
it does not inhibit the FeN
Figure 11. Schematic diagram of Fe-phen/C preparation and its catalyzed reduction reaction of nitroaromatics. Reprinted with permission from Ref. [42]. Copyright 2015, American Chemical Society.

4.2. Hydrogenation of Nitroarenes
Beller et al. developed a classic iron catalyst (Fe-phen/C) derived from pyrolyzing the mixture of Fe(OAc)2, 1,10-phenanthroline and carbon powder (Figure 11) [42]. The prepared catalyst exhibits high chemo-selectivity toward the reduction of various nitroarenes to corresponding aromatic amines with hydrazine hydrate as a hydrogen source. Subsequently, the catalytic activity toward the reduction of nitroarenes of Fe-phen/C was further investigated by the same group using H2 or HCOOH as a hydrogen source [57,80]. The FeN4 sites on the iron oxide surface are the source of the unique catalytic activity of this catalyst. Meanwhile, iron oxide can also play a minor role in the reduction reaction if it does not inhibit the FeN4 sites of the catalyst.

It is well known that nitrogen atoms act as basic sites in N-doped nanocarbon-supported iron catalysts, which can improve their hydrogenation performance [81]. Melamine was mixed with MIL-101(Fe) to improve the nitrogen content, and the resultant mixture was pyrolyzed at 700 °C to obtain Fe/Fe2O3@N5PC-700-1 [54]. This material exhibits excellent chemical selectivity towards the hydrogenation of nitro compounds, and the turnover frequency (TOF) reaches 8898 h⁻¹, which is 100 times higher than that of
reported similar catalysts [82]. Meanwhile, the nitrogen sites on the catalyst surface can effectively capture nitrobenzene and aniline to further improve the catalytic activity of this material.

In 2019, a novel iron single-atom catalyst Fe$_1$/N-C was prepared by immersing the template SBA-15 into the mixture of ferric nitrate and glucosamine, which was then calcinated at inert atmosphere before acid etching [70]. The prepared Fe$_1$/N-C exhibits excellent activity for the transfer hydrogenation of nitroarenes to amines with hydrazine as a hydrogen source. A series of characterization confirmed that the formation of FeN$_4$ active sites in Fe$_1$/N-C, and the pathway for hydrogenation of nitroarene in the presence of FeN$_4$ sites was investigated [83].

In 2020, Fe$_{SA}$/Fe$_2$O$_{3ACs}$/NPC that both contain FeN$_4$ sites and Fe$_2$O$_3$ clusters was fabricated by the pyrolysis of Fe-ZIF at 900 °C, which was then annealed naturally [43]. Compared with Fe$_{SA}$ and Fe NPs, Fe$_{SA}$/Fe$_2$O$_{3ACs}$/NPC shows the highest activity towards hydrogenation of nitroarenes (TOF up to 1923 h$^{-1}$), owing to the synergistic effect between Fe$_{SA}$ and Fe$_2$O$_{3ACs}$. Based on the DFT results, Fe$_{SA}$ reduces the overall barrier for hydrazine to decompose into hydrogen, and then under the catalysis of Fe$_2$O$_{3ACs}$, the hydrogen further participates in the hydrogenation reaction of nitrobenzene.

In 2022, our group developed an aniline modified ZIF-derived N-doped carbon iron single-atom catalyst (Fe$_{SA}$@NC-20A) with 2.4 wt.% Fe loading (Figure 12) [84]. This catalyst displays excellent catalytic performance on the selective hydrogenation of nitroarenes, with N$_2$H$_4$·H$_2$O as the reducing agent (TOF up to 1727 h$^{-1}$, more than 10 runs). This strategy also exhibits great potential to be applied to the synthesis of complex amines and drugs. According to DFT calculations and control experiments, the N-H activation of N$_2$H$_4$·H$_2$O is confirmed as the rate determine step, and FeN$_4$ sites in Fe$_{SA}$@NC-20A are considered the active sites for this reaction.

![Figure 12. The preparation process of Fe$_{SA}$@NC-20A. Reprinted with permission from Ref. [84]. Copyright 2022, Springer Nature.](image-url)

Recently, a mesoporous carbon (MC) support was prepared by hydrothermal reaction of citric acid and magnesium citrate, which was then loaded by potassium ferrocyanide through calcination to form NMC-Fe [85]. The prepared NMC-Fe could selectively mediate the reduction of nitro aromatics into azo compounds using hydrazine hydrate as a hydrogen source (Scheme 3), which was due to the formation of Fe-N complex in the NMC-Fe catalyst.
Recently, a mesoporous carbon (MC) support was prepared by hydrothermal reaction of citric acid and magnesium citrate, which was then loaded by potassium ferrocyanide through calcination to form NMC–Fe. The preparation applied in this work provides new insights to synthesize uniform -shaped metal nanoparticle catalysts from MOFs.

4.3. Others

In 2016, the group of Fu applied an iron catalyst (Fe-L1/C-800, the same catalyst in ref. [77]) to achieve the transfer hydrogenation of furfural (FF) to furfuryl alcohol (FFA) with a selectivity of 83.0% and a conversion rate of 91.6% [86]. Moreover, the catalyst can be reused five times, and finally deactivates due to the destruction of the Fe-N bond, the formation of crystalline Fe$_2$O$_3$ phase and the change of pore structure. In 2018, they continued to study the same catalyst for the selective cracking of C-O bonds in lignin model compounds (Scheme 4). In the presence of Fe-L1/C-800, the α-O-4 linkage of lignin model compounds is directly hydrolyzed to phenol and toluene, with yields of 95% and 90%, respectively [68]. In the occasion of the β-O-4 compounds, the presence of vicinal -OH group is required. Although monomers are not detected during the Fe-L1/C-800-catalyzed lignin pyrolysis process, its selectivity to aromatic hydrocarbons is still much higher than that of noble metal catalysts.

Scheme 3. NMC-Fe-catalyzed reduction coupling of nitroaromatics to form azo compounds.

Scheme 4. Selective hydrogenolysis of the C-O bonds in α-O-4 and β-O-4 lignin models over Fe-N/C catalyst.
5. Cascade Reactions

Cascade reaction is considered as a sustainable and environmentally friendly tool for the synthesis of new drugs and natural products, owing to its step and atom economy, simple operation process, lesser amount of solvent and reagents used and minimized waste emission. Therefore, the preparation of secondary amines, nitriles, unnatural amino acids and \(N\)-arylsulfonamides has been explored via a cascade reaction catalyzed by nanocarbon-supported iron catalysts.

5.1. Dehydration-Oxidation Reactions

Li et al. prepared 2,5-diformylfuran (DFF) from fructose via one-pot two-step process with 5-hydroxymethylfurfural (HMF) as the intermediate (Figure 13a) [87]. This transformation could be achieved by an octahedral Fe/C-S catalyst, which was produced from the pyrolysis of sulfur powder-doped Fe-based MOF (Figure 13b). The doping of sulfur results in more acidic sites that promote the dispersion of iron species, which is beneficial for the dehydration of fructose and the oxidation of HMF to DFF. The high catalytic activity and selectivity for Fe/C-S were also attributed to the strong adsorption of HMF and weak interaction of DFF with catalyst, respectively. Furthermore, the strategy for catalyst preparation applied in this work provides new insights to synthesize uniform-shaped metal nanoparticle catalysts from MOFs.

![Figure 13. (a) One-pot synthesis of DFF from glucose. (b) Synthetic strategy for Fe/C-S catalysts (The illustration proposed the possible structure in the catalyst). Reprinted with permission from Ref. [87]. Copyright 2017, Royal Society of Chemistry.](image)

5.2. N-Alkylation Reactions

Our group prepared a stable and recoverable N, S-codoped Fe\(_{20}\)-SA@NSC catalyst with a high iron loading of 2.51 wt.% [66], which can catalyze the \(N\)-alkylation of amines and alcohols with high selectivity and efficiency under solvent free conditions (TOF up to \(13.9\, \text{h}^{-1}\)) (Figure 14). According to the results of HAADF-STEM, XAFS and DFT calculations, the single atom site Fe\(_1\)-N\(_4\)S\(_1\) was formed in Fe\(_{20}\)-SA@NSC with high electron density, which not only enhances the C-H bond activation of alcohols, but also improves the hydrogen borrowing ability.

![Figure 14. Schematic diagram of the preparation of N, S-codoped Fe\(_{20}\)-SA@NSC and its catalytic application for synthesizing N-alkylation of aromatic amines under solvent free conditions. Reprinted with permission from Ref. [66]. Copyright 2021, Royal Society of Chemistry.](image)
Figure 14. Schematic diagram of the preparation of N, S-codoped Fe\textsubscript{20}-SA@NSC and its catalytic application for synthesizing N-alkylation of aromatic amines under solvent-free conditions. Reprinted with permission from Ref. [66]. Copyright 2021, Royal Society of Chemistry.

In 2014, Beller et al. synthesized Fe\textsubscript{2}O\textsubscript{3}/NGr@C by their reported method for the N-alkylation of benzaldehyde with nitroarenes to prepare secondary amines [88]. In this work, anilines were formed in situ from the hydrogenation of nitroarenes, and underwent a condensation reaction with aldehydes to afford imines, which were then reduced to afford N-alkylation amines (Scheme 5a). This method shows atom economy and environmental friendliness, providing an important application prospect for the industrial production for secondary amines. In 2017, they continued to study the application of Fe\textsubscript{2}O\textsubscript{3}/NGr@C catalyst in the fabrication of N-methylated amines from nitroarene and paraformaldehyde without a hydrogen source [89]. The paraformaldehyde in this work acts as both a hydrogen source and a methylaing agent. In addition to structurally different substrates, some drugs and fluorescent molecules containing nitro groups can also well undergo this strategy to afford corresponding N-methylated amines (Scheme 5b), including nimodipine, cilnidipine, nicardipine, nimesulide, rhodamine derivatives and fluorenone.

\[ R^1\text{-NO}_2 + R^2\text{-CHO} \xrightarrow{\text{Fe}_2\text{O}_3/\text{NGr@C}} R^1\text{-HN}_2R^2 \]

Selected examples:

- \[
\begin{array}{c}
\text{Cl} \quad \text{75%} \\
\text{SMe} \\
\text{NH} \\
\end{array}
\]

- \[
\begin{array}{c}
\text{HN} \\
\text{Ph} \\
\end{array}
\]

- \[
\begin{array}{c}
\text{HN} \\
\text{Ph} \\
\end{array}
\]

Scheme 5. Cont.
were performed to investigate the catalytic mechanism, the results of which indicate that (Scheme 6b). Both the nitrogen-doped graphene layer-supported Fe\(_2\)O\(_3\) nanoparticles and FeN\(_x\) sites, which is conducive to the formation of stable FeN\(_4\) active sites. The catalyst facilitates the absorption of oxygen and the transportation of reactants in the catalytic process, and maintains a high catalytic activity after being reused six times, which plays an important role in exploring the conversion of renewable biomass resources (bio-based primary alcohols) into fine chemicals (nitriles).

In 2018, the nitriles and amides were prepared via the tandem reaction of aldehydes and ammonia in the presence of Fe\(_2\)O\(_3\)-N/C [90]. The aldehydes and ammonia first undergo condensation reaction to generate imines, which are oxidized to desired nitriles (Scheme 6a). An additional hydrolysis process is required for the formation of amides (Scheme 6b). Both the nitrogen-doped graphene layer-supported Fe\(_2\)O\(_3\) nanoparticles and Fe-N interactions are found to contribute to the activity of Fe\(_2\)O\(_3\)-N/C. Moreover, gram scale synthesis is realized in this green strategy, and the Fe\(_2\)O\(_3\)-N/C can be reused for several times, indicating the potential industrial application of this work.

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In 2019, Fe-Fe\(_2\)C@NC, composed of a N-doped carbon layer surrounded Fe-Fe\(_2\)C nanoparticles and FeN\(_x\) sites, was prepared by Song et al., which was then applied in the oxidative cyclization reaction between amines and aldehydes to efficiently synthesize quinolines and quinazolinones [58]. A series of characterization and control experiments were performed to investigate the catalytic mechanism, the results of which indicate that the Fe-Fe\(_2\)C nanoparticles and FeN\(_x\) sites in Fe-Fe\(_2\)C@NC have a synergistic catalytic effect in catalyzing this cyclization reaction. This strategy provides a convenient and sustainable method for obtaining a set of N-heterocycles with pharmaceutical action.

\[ \text{(Scheme 5.)} \]

\[ \text{(b) Ar-NO}_2 + (\text{CH}_2\text{O})_{100} \xrightarrow{\text{Fe}_2\text{O}_3/\text{NGr@C}} \text{Me} \]

\[ \text{Ar-N}_2\text{Me} \]

**Selected examples**

- 92% success: 
  \[ \text{Me} \]

- 79% success: 
  \[ \text{O} \]

- 70% success: 
  \[ \text{O} \]

- 87% success: 
  \[ \text{O} \]

- 88% success: 
  \[ \text{O} \]

- 85% success: 
  \[ \text{OH} \]

**Scheme 5.** (a) The preparation of secondary amines catalyzed by Fe\(_2\)O\(_3\)-N/C. (b) The synthesis of N-methylated amines catalyzed by Fe\(_2\)O\(_3\)-NGr@C. The cascade reaction of nitroarenes and aldehydes for the synthesis of N-alkylation amines.

5.3. Oxidative Coupling Reactions

In 2018, some of us synthesized a single-atom catalyst Fe\(_1\)-N-C by calcining ZIFs to achieve the conversion of a wide range of primary alcohols to nitriles under mild conditions for the first time (Figure 15) [91]. In the preparation process of the catalyst, benzyl amine is introduced to make the obtained catalysts with higher nitrogen contents, and modify the morphology, crystal structure and size of ZIFs, which is conducive to the formation of active FeN\(_4\) sites. The catalyst facilitates the absorption of oxygen and the transportation of reactants in the catalytic process, and maintains a high catalytic activity after being reused six times, which plays an important role in exploring the conversion of renewable biomass resources (bio-based primary alcohols) into fine chemicals (nitriles).

In 2019, Fe-Fe\(_2\)C@NC, composed of a N-doped carbon layer surrounded Fe-Fe\(_2\)C nanoparticles and FeN\(_x\) sites, was prepared by Song et al., which was then applied in the oxidative cyclization reaction between amines and aldehydes to efficiently synthesize quinolines and quinazolinones [58]. A series of characterization and control experiments were performed to investigate the catalytic mechanism, the results of which indicate that the Fe-Fe\(_2\)C nanoparticles and FeN\(_x\) sites in Fe-Fe\(_2\)C@NC have a synergistic catalytic effect in catalyzing this cyclization reaction. This strategy provides a convenient and sustainable method for obtaining a set of N-heterocycles with pharmaceutical action.
Selected examples

Scheme 6. (a) The tandem reaction of aldehydes and ammonia to prepare nitriles. (b) The synthesis of amides from the reaction of aldehydes and ammonia.

Scheme 6. (a) The tandem reaction of aldehydes and ammonia to prepare nitriles. (b) The synthesis of amides from the reaction of aldehydes and ammonia.

Figure 15. (a) Synthesis of Fe$_1$-N-C catalyst (The illustration presented the possible structure of the catalyst). (b) Fe$_1$-N-C catalyzed ammoxidation of alcohols to form nitriles. $^a$2 MPa air, 130 °C. Reprinted with permission from Ref. [91]. Copyright 2022, Springer Nature.
Natural woods are an abundant biomass with hierarchical structure and good mechanical properties, which have been applied as porous carbon supports to immobilize iron single atoms for the formation of iron-based single atom catalyst (SAC) (Figure 16) [92]. The obtained iron-based SAC shows excellent performance in three-component oxidative cyclization to afford various quinolines from anilines and ketones under mild conditions. In addition, this iron-based SAC exhibits better activity than traditional catalysts, such as Pd/C, Fe/C and FeCl₃. The DFT calculations were performed to identify the active sites in iron-based SAC, and the FeN₄ sites were found with lower reaction barriers than Fe-C₁N₃ and Fe-C₂N₂. Therefore, the excellent catalytic activity of iron-based SAC can be attributed to the weak desorption energy between FeN₄ and products, and the increased exposure of active sites resulted from hierarchically porous carbon plates.

Figure 16. Schematic of the preparation of carbon-based single-atom catalyst from natural wood. Reprinted with permission from Ref. [92]. Copyright 2019, Wiley.

6. Others

Acceptorless dehydrogenation can produce valuable intermediates while generating molecular hydrogen, which is known as a green energy resource. Based on this, Balaraman et al. prepared a Fe-L₁@EGO-900 catalyst with iron oxides as the outer shell and iron carbide as the inner core for acceptorless dehydrogenation of N-heterocycles, amines and alcohols (Scheme 7) [41]. However, other iron catalysts prepared from traditional supports, such as Al₂O₃, SiO₂, CeO₂ and TiO₂, failed to undergo this reaction under similar experimental conditions. This is due to the fact that 1,10-phenanthroline (L₁) with broad π area is applied to prepare Fe-L₁@EGO-900, which enables the catalyst to better recognize and bind substrate. Furthermore, this catalyst can be reused four times without a significant decrease in activity, showing potential for practical application.

In 2022, Beller et al. prepared Fe-Cellulose-1000 with metallic iron as the active site by pyrolyzing the mixture of cellulose and Fe(NO₃)₃·9H₂O at 1000 °C [93]. This material breaks through the limitations of the acid-required hydrogen-deuterium exchange reaction, and can selectively catalyze the deuteration of the locations that are not prone to electrophilic substitution reactions (Figure 17). In the reaction pathway of catalytic deuteration, the iron oxides in Fe-Cellulose-1000 can be reduced in situ to metallic iron under hydrogen pressure, which further promotes the homolytic splitting of the deuteration reagent (D₂O). The generated •OD radicals are activated and adsorbed on the surface of the catalyst in the form of D⁺ and •OD, and the former one can selectively substitute hydrogen atom on the benzene ring. Therefore, the Fe-Cellulose-1000 can promote highly selective deuteration reaction of aniline, indole, phenol and other heterocyclic compounds, and there is no obvious activity loss of Fe-Cellulose-1000 after five times of recycle. Furthermore,
this catalyst can be applied to the preparation of kilogram-grade deuterated compounds, providing the possibility of industrial production.

\[
\text{(a) } \begin{array}{c}
\text{Fe-L}_{1}\@\text{EGO-900} \\
\text{FeCl}_2 \cdot 4\text{H}_2\text{O, terephthalic acid, 1,4-diazabicyclo [2,2,2] octane (DABCO) at 800 °C} \\
\end{array} + n\text{H}_2
\]

Selected examples

\[
\begin{array}{ccc}
\text{N} & \text{N} & \text{Me} \\
88\% & 78\% & 58\%
\end{array}
\]

\[
\text{(b) } \begin{array}{c}
\text{R} = \text{NH}_2 \\
\text{Fe-L}_{1}\@\text{EGO-900} \\
\text{I-ButOK, mesitylene} \\
\text{Ar, 145 °C} \\
\text{R} = \text{N} = \text{R} + \text{H}_2
\end{array}
\]

Selected examples

\[
\begin{array}{ccc}
\text{N} & \text{Me} & \text{Me} \\
90\% & 71\% & 59\%
\end{array}
\]

\[
\text{(c) } \begin{array}{c}
\text{O} \\
\text{Fe-L}_{1}\@\text{EGO-900} \\
\text{I-ButOK, n-octane} \\
\text{Ar, } \Delta \\
\text{O} + \text{H}_2
\end{array}
\]

Selected examples

\[
\begin{array}{ccc}
\text{Me} & \text{H} & \text{H} \\
91\% & 55\% & 21\%
\end{array}
\]

Scheme 7. Fe-L_{1}@EGO-900 catalyzed acceptorless dehydrogenation of (a) N-heterocycles, (b) amines and (c) alcohols.

Figure 17. Selective deuteration of (hetero)arenes over Fe-Cellulose-1000. Reprinted with permission from Ref. [93]. Copyright 2022, Springer Nature.

Another efficient catalyst Fe@NC-800 for acylation reaction was reported by Jia et al., which was prepared by pyrolyzing the Fe-DABCO-MOF formed by self-assembly of FeCl_2·4H_2O, terephthalic acid and 1,4-diazabicyclo [2,2,2] octane (DABCO) at 800 °C (Figure 18) [94]. In addition to provide nitrogen source, the incorporation of DABCO can also facilitate the formation of highly graphitized materials and inhibit iron agglomeration. The excellent catalytic performance of this catalyst is mainly attributed to the electronic effect of the graphic layer and encapsulation of iron particles by the graphic layer, which will promote the stabilization of the iron species.
In 2021, our group constructed a nitrogen-doped carbon supported iron-based catalyst Fe@CN-Zn using iron nitrate as the iron source, zinc nitrate as the pore forming agent, and melamine and ethyl cellulose as the nitrogen source and carbon source, respectively [50]. In this work, carbene species were generated from diazoacetate in the presence of Fe@CN-Zn, and then further reacted with amines to afford corresponding amino acid derivatives (Figure 19). The N-doped carbon decreased the electron density of Fe/FeO nanoparticles in Fe@CN-Zn [95], which is beneficial for the formation of intermediate A. Meanwhile, the dope of nitrogen afforded more Lewis base sites, improving the transfer of proton during the reaction process. The active Fe@CN-Zn catalyst can be recycled four times without significant activity loss.

7. Summary and Outlook

This review focuses on organic reactions catalyzed by carbon-based iron materials, such as oxidation, reduction and tandem reactions, in which the introduction strategies of iron into carbon materials and the structure and activity relationship between carbon-based iron catalysts and organic reactions are summarized. Despite the great development in this field, challenges and opportunities for the widespread application of iron-doped carbon materials still exist.

The homogeneity and tunability of iron sites are the basis for the high catalytic performance of carbon-based iron catalysts. There is still a lack of effective means to regulate and determine the coordination environment of iron sites. A feasible solution is anchoring single iron atoms on nitrogen-doped carbon, forming $\text{FeN}_x$ sites with similar coordination environments, which can be detected by X-ray absorption near edge structure (XANES). Nevertheless, limited approaches have been demonstrated for fine-tuning $\text{FeN}_x$ sites. At the same time, the current characterization of XANES is the weighted average of the
coordination environment of all iron sites, so the homogeneity of iron sites is actually not high.

Compared with homogeneous iron catalysis, the application range of carbon-supported iron catalysts in organic synthesis is very limited. There are two main reasons for this:

1. The poor homogeneity and tunability of iron sites in these catalysts limits its application in complex and delicate organic synthesis, such as asymmetric synthesis. The investigation of efficient strategies for improving the homogeneity or tuning the coordination environment of iron sites is desirable.

2. Since most organic chemists are not proficient in designing and preparing such materials, more chemists that are specialized in organic synthesis, catalysis and materials ought to undertake related cooperation and innovation in this field, in order to expand its application range and depth.

Finally, carbon-based iron catalysts also offer more new possibilities for organic synthesis. For example, these catalysts exhibit excellent catalytic activity for the activation of O₂, owing to porous structure and enzyme-like iron sites, so they can enable many efficient green oxidation processes.

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References
1. Rodionov, I.A.; Zvereva, I.A. Photocatalytic activity of layered perovskite-like oxides in practically valuable chemical reactions. Russ. Chem. Rev. 2016, 85, 248–279. [CrossRef]
2. Ju, S.; Shin, G.; Lee, M.; Koo, J.M.; Jeon, H.; Ok, Y.S.; Hwang, D.S.; Hwang, S.Y.; Oh, D.X.; Park, J. Biodegradable chito-beads replacing non-biodegradable microplastics for cosmetics. Green Chem. 2021, 23, 6953–6965. [CrossRef]
3. Rydel-Ciszek, K.; Pazceśniak, T.; Zaborniak, I.; Bloniarz, P.; Surmacz, K.; Sobkowiak, A.; Chmielarz, P. Iron-Based Catalytically Active Complexes in Preparation of Functional Materials. Processes 2020, 8, 1683. [CrossRef]
4. Shesterkina, A.A.; Kustov, L.M.; Strekalova, A.A.; Kazansky, V.B. Heterogeneous iron-containing nanocatalysts—Promising systems for selective hydrogenation and hydrogenolysis. Catal. Sci. Technol. 2020, 10, 3160–3174. [CrossRef]
5. Shang, R.; Ilies, L.; Nakamura, E. Iron-Catalyzed C-H Bond Activation. Chem. Rev. 2017, 117, 9086–9139. [CrossRef]
6. Furstner, A. Iron Catalysis in Organic Synthesis: A Critical Assessment of What It Takes to Make This Base Metal a Multitasking Champion. ACS Cent. Sci. 2016, 2, 778–789. [CrossRef] [PubMed]
7. Wei, D.; Darcel, C. Iron Catalysis in Reduction and Hydrometalation Reactions. Chem. Rev. 2019, 119, 2550–2610. [CrossRef]
8. Bauer, I.; Knolker, H.J. Iron catalysis in organic synthesis. Chem. Rev. 2015, 115, 3170–3387. [CrossRef] [PubMed]
9. Bertini, I.; Gray, H.B.; Lippard, S.J.; Valentine, J.S. Bioinorganic Chemistry; University Science Books: Mill Valley, CA, USA, 1994.
10. Wang, Q.; Tao, H.L.; Li, Z.Q.; Wang, G.X. Effect of iron precursor on the activity and stability of PtFe/C catalyst for oxygen reduction reaction. J. Alloy Compd. 2020, 814, 152212. [CrossRef]
11. Wu, Q.S.; Yang, H.P.; Kang, L.; Gao, Z.; Ren, F.F. Fe-based metal-organic frameworks as Fenton-like catalysts for highly efficient degradation of tetracycline hydrochloride over a wide pH range: Acceleration of Fe (II)/Fe (III) cycle under visible light irradiation. Appl. Catal. B-Environ. 2020, 263, 118282. [CrossRef]
12. Hedstrom, A.; Lindstedt, E.; Norby, P.O. On the oxidation state of iron in iron-mediated C-C couplings. J. Organomet. Chem. 2013, 748, 51–55. [CrossRef]
13. Sun, X.B.; Hansen, T.; Poater, J.; Hamlin, T.A.; Bickelhaupt, F.M. Rational design of iron catalysts for C-X bond activation. J. Comput. Chem. 2022, in press. [CrossRef] [PubMed]
14. Zuo, W.W.; Lough, A.J.; Li, Y.F.; Morris, R.H. Amine(imine)diphosphine Iron Catalysts for Asymmetric Transfer Hydrogenation of Ketones and Imines. Science 2013, 342, 1080–1083. [CrossRef]
15. Morris, R.H. Exploiting Metal-Ligand Bifunctional Reactions in the Design of Iron Asymmetric Hydrogenation Catalysts. Accounts Chem. Res. 2015, 48, 1494–1502. [CrossRef]
16. Raji, M.; Mirbagheri, S.A.; Ye, F.; Dutta, J. Nano zero-valent iron on activated carbon cloth support as Fenton-like catalyst for efficient color and COD removal from melanoidin wastewater. Chemosphere 2021, 263, 127945. [CrossRef]
17. Cui, X.J.; Li, Y.H.; Bachmann, S.; Scalone, M.; Surkus, A.E.; Junge, K.; Topf, C.; Beller, M. Synthesis and Characterization of Iron-Nitrogen-Doped Graphene/Core-Shell Catalysts: Efficient Oxidative Dehydrogenation of N-Heterocycles. *J. Am. Chem. Soc.* 2015, 137, 10652–10658. [CrossRef]

18. Varma, R.S. Biomass-Derived Renewable Carbonaceous Materials for Sustainable Chemical and Environmental Applications. *ACS Sustain. Chem. Eng.* 2019, 7, 6458–6470. [CrossRef]

19. Kramer, S.; Hejo, P.; Rasmussen, K.H.; Kegnæs, S. Silylative Pinacol Coupling Catalyzed by Nitrogen-Doped Carbon-Encapsulated Nickel/Cobalt Nanoparticles: Evidence for a Silyl Radical Pathway. *ACS Catal.* 2017, 8, 754–759. [CrossRef]

20. Lin, Y.; Ju, J.; Zhang, X.; Fang, J.; Lu, G.-P.; Huang, H. Carbohydrate-derived porous carbon materials: An ideal platform for green organic synthesis. *Chin. Chem. Lett.* 2022, 33, 186–196. [CrossRef]

21. Sun, K.; Shan, H.; Lu, G.P.; Cai, C.; Beller, M. Synthesis of N-Heterocycles via Oxidant-Free Dehydrocyclization of Alcohols Using Heterogeneous Catalysts. *Angew. Chem. Int. Ed. Eng.* 2021, 60, 25188–25202. [CrossRef] [PubMed]

22. Lam, E.; Luong, J.H.T. Carbon Materials as Catalyst Supports and Catalysts in the Transformation of Biomass to Fuels and Chemicals. *ACS Catal.* 2014, 4, 3393–3410. [CrossRef]

23. Borchardt, L.; Zhu, Q.-L.; Casco, M.E.; Berger, R.; Zhuang, X.; Kaskel, S.; Feng, X.; Xu, Q. Toward a molecular design of porous carbon materials. *Mater. Today* 2017, 20, 592–610. [CrossRef]

24. Sun, K.; Shan, H.; Ma, R.; Wang, P.; Neumann, H.; Lu, G.P.; Beller, M. Catalytic oxidative dehydrogenation of N-heterocycles with nitrogen/phosphorus co-doped porous carbon materials. *Chem. Sci.* 2022, 13, 6685–6672. [CrossRef] [PubMed]

25. Su, T.Y.; Lu, G.P.; Sun, K.K.; Zhang, M.; Cai, C. ZIF-derived metal/N-doped porous carbon nanocomposites: Efficient catalysts for organic transformations. *Catal. Sci. Technol.* 2022, 12, 2106–2121. [CrossRef]

26. Jiao, L.; Yan, H.; Wu, Y.; Gu, W.; Zhu, C.; Du, D.; Lin, Y. When Nanozymes Meet Single-Atom Catalysis. *Angew. Chem. Int. Ed. Engl.* 2020, 59, 2565–2576. [CrossRef]

27. Lin, Y.; Wang, F.; Yu, J.; Zhang, X.; Lu, G.-P. Iron single-atom anchored N-doped carbon as a 'laccase-like' nanzyme for the degradation and detection of phenolic pollutants and adrenaline. *J. Hazard. Mater.* 2021, 425, 127763. [CrossRef]

28. Rana, S.; Biswas, J.P.; Paul, S.; Paik, A.; Maiti, D. Organic synthesis with the most abundant transition metal-iron: From rust to multitasking catalysts. *Chem. Soc. Rev.* 2021, 50, 243–472. [CrossRef]

29. Wang, X.; Zhang, X.; Zhang, Y.; Wang, Y.; Sun, S.-P.; Wu, W.D.; Wu, Z. Nanostructured semiconductor supported iron catalysts for heterogeneous photo-Fenton oxidation: A review. *J. Mater. Chem. A* 2020, 8, 15513–15546. [CrossRef]

30. Raya-Barndamar, N.J.; Neidig, M.L. Additive and Counterion Effects in Iron-Catalyzed Reactions Relevant to C-C Bond Formation. *ACS Catal.* 2019, 9, 5400–5417. [CrossRef]

31. Bailly, B.; Vento, D.C.G.A.; Silva, A.M.S. Iron: A Worthy Contender in Metal Carbene Chemistry. *ACS Catal.* 2020, 10, 10096–10116. [CrossRef]

32. Sears, J.D.; Neate, P.G.N.; Neidig, M.L. Intermediates and Mechanism in Iron-Catalyzed Cross-Coupling. *J. Am. Chem. Soc.* 2018, 140, 11872–11883. [CrossRef] [PubMed]

33. Bakas, N.J.; Neidig, M.L. Additive and Counterion Effects in Iron-Catalyzed Reactions Relevant to C-C Bond Formation. *ACS Catal.* 2021, 11, 8493–8503. [CrossRef]

34. Cassani, C.; Bergonzini, G.; Wallentin, C.-J. Active Species in Iron-Catalyzed Reactions Relevant to C-C Bond Formation. *ACS Catal.* 2021, 11, 9449–9455. [CrossRef]

35. Damiano, C.; Sonzini, P.; Gallo, E. Iron catalysts with N-ligands for carbene transfer of diazo reagents. *Chem. Soc. Rev.* 2020, 49, 4867–4905. [CrossRef]

36. Balaraman, E.; Nandakumar, A.; Jaiswal, G.; Sahoo, M.K. Iron-catalyzed dehydrogenation reactions and their applications in sustainable energy and catalysis. *Chem. Sci. Technol.* 2017, 7, 3177–3195. [CrossRef]

37. Damiano, C.; Sonzini, P.; Gallo, E. Iron catalysts with N-ligands for carbene transfer of diazo reagents. *Chem. Soc. Rev.* 2020, 49, 4867–4905. [CrossRef]

38. Batista, V.F.; Pinto, D.C.G.A.; Silva, A.M.S. Iron: A Worthy Contender in Metal Carbene Chemistry. *ACS Catal.* 2020, 10, 10096–10116. [CrossRef]

39. Siers, J.D.; Neate, P.G.N.; Neidig, M.L. Intermediates and Mechanism in Iron-Catalyzed Cross-Coupling. *J. Am. Chem. Soc.* 2018, 140, 11872–11883. [CrossRef] [PubMed]

40. Bakas, N.J.; Neidig, M.L. Additive and Counterion Effects in Iron-Catalyzed Reactions Relevant to C-C Bond Formation. *ACS Catal.* 2021, 11, 8493–8503. [CrossRef]

41. Cassani, C.; Bergonzini, G.; Wallentin, C.-J. Active Species in Iron-Catalyzed Reactions Relevant to C-C Bond-Forming Cross-Coupling Reactions. *ACS Catal.* 2016, 6, 1640–1648. [CrossRef]

42. Bailly, B.; Thomas, S.P. Iron-catalyzed reduction of carbonyls and olefins. *RSC Adv.* 2011, 1, 1435–1445. [CrossRef]

43. Liu, P.; Gao, S.; Wang, Y.; Huang, Y.; He, W.; Huang, W.; Luo, J. Carbon nanocages with Co/N-doped carbon outer shell as electromagnetic wave absorption materials. *Chem. Eng. J.* 2020, 381, 122653. [CrossRef]

44. Yang, L.Y.; Feng, Y.; Yu, D.B.; Qiu, J.H.; Zhang, X.F.; Dong, D.H.; Yao, J.F. Design of ZIF-based CNFs wrapped porous carbon with hierarchical pores as electrode materials for supercapacitors. *J. Phys. Chem. Solids* 2019, 125, 57–63. [CrossRef]

45. Zhang, X.; Fan, Q.Y.; Yang, H.; Xiao, H.Y.; Xiao, Y.H. Metal-organic framework assisted synthesis of nitrogen-doped hollow carbon materials for enhanced supercapacitor performance. *New J. Chem.* 2018, 42, 17389–17395. [CrossRef]

46. Jaiswal, G.; Landge, V.G.; Jagadeesan, D.; Balaraman, E. Iron-based nanocatalyst for the acceptorless dehydrogenation reactions. *Nat. Commun.* 2017, 8, 2147–2159. [CrossRef] [PubMed]

47. Jagadeesh, R.V.; Steenkerk, T.; Surkus, A.-E.; Junge, H.; Junge, K.; Beller, M. Hydrogenation using iron oxide-based nanocatalysts for the synthesis of amines. *Nat. Protoc.* 2015, 10, 548–557. [CrossRef]

48. Yun, R.; Zhan, F.; Li, N.; Zhang, B.; Ma, W.; Hong, L.; Sheng, T.; Du, L.; Zheng, B.; Liu, S. Fe Single Atoms and Fe2O3 Clusters Liberated from N-Doped Polyhedral Carbon for Chemoselective Hydrogenation under Mild Conditions. *ACS Appl. Mater. Inter.* 2020, 12, 34122–34129. [CrossRef] [PubMed]

49. Li, J.K.; Jiao, L.; Wegener, E.; Richard, L.L.; Liu, E.S.; Zitolo, A.; Sougrati, M.T.; Mukerjee, S.; Zhao, Z.P.; Huang, Y.; et al. Evolution Pathway from Iron Compounds to Fe-1(II)-N-4 Sites through Gas-Phase Iron during Pyrolysis. *J. Am. Chem. Soc.* 2020, 142, 1417–1423. [CrossRef] [PubMed]

50. Deng, B.; Liu, Z.; Peng, H. Toward Mass Production of CVD Graphene Films. *Adv. Mater.* 2019, 31, 1800996. [CrossRef] [PubMed]
