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Homogenous meets Heterogenous and Electro-Catalysis: Iron-nitrogen molecular complexes within carbon materials for catalytic applications

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Abstract: High activity, selectivity and recyclability are crucial parameters in the design of performant catalysts. Furthermore, depletion of platinum-group metals (PGM) drives further research towards highly available metal-based catalysts. In this framework, iron-based active sites supported on nitrogen-doped carbon materials (Fe/N@C) have been explored to tackle important applications in organic chemistry, for both oxidation and reduction of C-O/C-N bonds, as well as in electrocatalysis for energy applications. This versatile reactivity makes them ideal substitutes to PGM-based catalysts, being based on abundant elements. Despite important advances in material science and characterisation techniques allowing the analysis of heterogeneous/electro- catalysts at the atomic scale, the nature of the catalytically active sites in Fe/N@C remains elusive. Most recent

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theoretical studies point at individual FeN_x single sites as the origin of the catalytic activity. Although their identification is still challenging with current technology, establishing their real nature will foster further research on these PGM-free and redox-polyvalent catalysts. In this review, we provide an overview of their applications in both thermal and electrochemical processes. Throughout the review, we highlight the different characterisation techniques employed to gain insight into the catalyst's active sites.

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1. Introduction

Climate change is now on the brink of causing irreversible damage unless greenhouse gas emissions are drastically reduced.^[1] At the Paris climate agreement in 2015, world leaders committed to take action against greenhouse gas emissions in order to keep the total increase of global warming below 2°C. Considering this ambitious goal, a fast shift from a fossil fuelbased society to a sustainable and renewable energy society is required. Many countries have announced bans for fossil-based vehicles, becoming effective as early as 2025 for some. All this does not only entail a rise in renewable energy generation through wind, solar or water power, but also with fuel cells and bioenergy. To balance out demand and supply as well as for future electric car technologies, efficient energy storage such as batteries and supercapacitors are also needed. With these drastic changes towards renewable energy technologies, sustainability must be kept in mind. A well-known definition of sustainability was defined in 1987 by the Brundtland Commission as "... development that meets the needs of the present without compromising the ability of future generations to meet their own needs".^[2] Many of the renewable energy technologies rely heavily on scarce and noble metals, such as lithium for batteries, gallium and germanium for solar cells, platinum group metals (PGM) for fuel cells.^[3] The most common electrocatalyst used in fuel cells is Pt supported on carbon. Yet, Pt is a scarce and expensive element with serious supply concerns as 75% of its world production comes from South Africa.^[4] Furthermore it exhibits relatively slow ORR (oxygen reduction reaction) kinetics, due to the formation of adsorbed -OH species,^[5] low long-time usage durability/stability and low tolerance for methanol or CO poisoning.^[6] Besides, greenhouse gas emissions from fossil carbon combustion can be mitigated using CO₂RR (CO₂ reduction reaction). In this process, CO₂ is converted in valuable products for the industry, such as syngas, CH₄, alcohols (MeOH and EtOH), formic acid, and formaldehyde.^[7] Up to date, many researchers reported selective electroreduction of CO₂ to CO and formic acid on noble metals (Ag, Au, Pd),^[8-10] despite the high stability of CO₂ molecule and the strong competition with hydrogen evolution reaction (HER) in aqueous electrolytes. As an approach to replace PGM-based electrocatalysts, metals such as Fe but also Cu, Mn and Ni were found as convenient alternatives. The potential of using these metals, in conjunction with nitrogen macrocyclic compounds, as ORR catalysts in alkaline electrolyte was first reported by Jasinski in 1964.^[11] They also have been mentioned for CO2RR.^[12] A variety of electrocatalysts have emerged from this, usually based on a carbon support, though the electrocatalytic activity of these materials depends on the metal itself, as well as on precursors used, the synthetic procedure and the metal content. Research in the 1990's has shown that Fe-based catalysts featured the most favourable electrocatalytic activity towards the ORR compared to other transition metals such as Mn, Ni, Zn, Mn and Cu.[13-15] Interestingly, the catalytic activity increases with rising metal content up to a certain limit, at which point the activity plateaus.^[14,16,17] This was explained by the increasing concentration of catalytic sites until all the nitrogen of the phenanthroline type is coordinated with metal and inactive metal clusters are formed.

These single iron sites supported to nitrogen-doped carbons materials (Fe/N@C) resemble metalloproteins such as the heme group in haemoglobin cytochrome c oxidase, an iron protoporphyrin responsible for oxygen-binding/transport in the human body.^[18] As significant example of heme-containing enzymes are cytochrome P450, with their active site containing a Fe³⁺-porphyrin cofactor.^[19] From a chemical perspective, they constitute exceptional catalysts for C-H oxidation using O2.[20] Since then, organic chemists have successfully mimicked and exploited the Fe-N cooperation via the elegant design of N-based pincer ligands for a myriad of oxidative and hydrogenative processes.^[21,22] The N-doping in carbon nanostructure is another common strategy towards the formation of efficient active sites by inducing charge redistribution around the heteroatom dopants. This alters O₂ chemisorption mode, weakens the O-O bonding and overall improves the catalytic activity for ORR [23] and CO2RR.^[24] Fe/N@C catalysts are particularly promising due to the balance between electrocatalytic activity and availability of resources. Overall, these bio-inspired catalysts constitute promising alternatives to precious metal-based catalysts, through a metal-ligand synergy. In this review we will cover the wide variety of electrochemical and organic reactions they have been shown to catalyse. In section 2 and 3, the introduction of Fe/N@C catalysts in diverse applications will be covered. Insights into the mechanisms of each application, and characterisation techniques will be discussed in Section 4.

2. FeN_x for electrocatalysis

Electrocatalytic reactions are characterised by an activation energy barrier between electrolyte and solid electrode that must be overcome by charge. In this review we will focus mainly on Fe/N@C for ORR and CO₂ reduction (CO₂RR), for those reaction Fe/N@C shows excellent performance even with lower content of Fe in the composites. ORR can follow either a 4- or a 2-electron pathway.^[5] The former, called full reduction, is always the favoured option to increase fuel cell efficiency. Indeed, the latter pathway also called partial reduction, forms H₂O₂, leading to membrane corrosion issues.^[6] With respect to CO₂RR, the final products are mostly dependent on the cathode employed during the reaction. The reaction could follow a 2-electron pathway and form syngas, 6-electron pathway for MeOH or 8/12-electron pathway when hydrocarbons are obtained.^[25] All reactions have

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been studied using noble-metal based electrocatalysts [26-29] but considering the scarce and expensive character of these type of catalysts together with the limited resources to very few regions of the globe, heteroatom doped carbon materials have emerged as promising alternatives for ORR and CO₂RR active catalysts.^{[30-} ^{32]} Carbon structures themselves can possess intrinsic catalytic activity, which can be modulated by adding dopants/defects. These affect electron density distribution, electron acceptor/donor ability, spin density, oxygen vacancies etc., to enhance both O₂ and CO₂ adsorption and dissociation, by reducing the energetic barriers.^[33] N is predominantly used as a dopant. Thanks to its electronegativity (3.04), higher than that of carbon (2.55), Ndoping causes positive charging of the carbon backbone.^[34] The addition of Fe in coordination nitrogen atoms supported on carbon forms highly efficient active sites promoting O₂ adsorption and thus boosting the electrocatalytic activity. Some of Fe-N-C catalysts have been synthesised by carbonising Fe-N₄-type macrocyclic complexes, whilst the carbonisation of inorganic precursors containing Fe and N is also widely applied.[35-38]

The catalytic activity of the electrocatalysts is commonly evaluated using a three-electrode electrochemical cell, which includes working electrode, reference electrode, counter electrode, and gas inlet. However, the experimental details need to be taken into consideration when comparing the catalysts performance, as different technical parameters vary in the literature (i.e. reference electrode selection, mass loading of electrocatalyst, data correction prior to extracting kinetic currents, etc.)^[39]Practical and useful protocols are under investigation for quantifying the active sites and accurate evaluate the catalytic performance of the catalysts, such as the kinetic isotope effect, site density, and turnover frequency, which were found to play significant role in determining the ORR performance of Fe/N@C catalyst in fuel cells.^[31,40–42]

2.1. Fe-N-C electro catalysts in ORR

2.1.1. Preparation by thermal treatment

Synthesis and assembly of Fe,N co-doped carbon nanostructures, such as carbon nanotubes, graphene and nanofibers, via pyrolysis methods were widely reported.^[43–47] For example, Li *et al.* synthesised N/Fe-doped nanotubes grown on carbon nanofibers using catkin, FeCl₃ and melamine (Figure 1a).^[26] The resulting electrocatalyst had a surface area of 461 m² g⁻¹, with 4.15 at% of N and 1.27 at% of Fe. They showed promising catalytic activity both in alkaline and acidic electrolytes. Liang, et al. reported an efficient method to produce N-doped carbon nanofibers (CNFs), using bacterial cellulose from a microbial fermentation process as precursor. The direct high temperature carbonisation and the consecutive NH₃ treatment were applied to facilitate the formation of N-CNTs.^[48] Their material had a high surface area of 916 m² g⁻¹ exhibiting a nanofibrous network structure and a nitrogen content of 5.8 at%. Testing in alkaline media revealed comparable performance to the one of Pt standard. Though the authors did not attribute any metal contribution to the good ORR performance, ICP atomic emission spectrometry revealed the presence of 0.01 wt% of metals (such as Fe and Co) resulting from the bacterial cellulose precursor, which most likely influenced the ORR activity via trace amount of metals, hence leading to a good catalytic activity. The synthesis of Fe/N@C from abundant precursors such as biomass via pyrolysis is a sustainable and efficient method to produce electrocatalysts with good electrocatalytic activity and long-term stability. Boiled egg white and FeCl₃ were used as a precursor to produce Fe/N-doped carbons via direct pyrolysis.^[49] Note that even trace amount of Fe could remarkable improve the catalytic activity. Indeed, Fe amounts undetectable by XPS but detectable by CN⁻ titration gave high ORR performance.^[50,51] Our group reported a Fe-N doped carbon hollow spheres using pyrrole as C and N precursor and FeCl₃ as source of iron. The hollow spheres were produced using silica as hard template. XPS demonstrated iron content as little as 0.2 at%, yet after poisoning the Fecentered catalytic sites using CN⁻ ions, the ORR activity largely decreased, demonstrating the remarkable contribution of the little amount of Fe in the catalyst.[52]

In addition to direct pyrolysis, hydrothermal carbonization (HTC) is another powerful and sustainable technique to promote the assembling of Fe/N@C. An HTC reaction takes place in a sealed autoclave in the presence of a bio-derived precursor (raw lignocellulose or a carbohydrate biopolymer) and H₂O as a solvent. The carbon materials are formed at moderate temperatures (200°C) and self-generated pressures.^[53] Fe/Ndoped nanofiber carbogels could be synthesised from glucosamine hydrochloride and ferrous gluconate with ultrathin Fe nanowires as template via HTC, followed by carbonisation.^[54] Hybrid carbogel containing iron nitride and N-doped graphene were also reported, made by HTC of graphene oxide and iron(II)phthalocyanine followed by a high temperature carbonisation (Figure 1b).^[55] High resolution TEM confirmed the presence of FeN sites in the final product, with 8.2 at% of nitrogen and 2.3 at% of iron. The hybrid material exhibited similar catalytic activity and better stability than a commercial platinum standard in alkaline media. The authors attributed this to the synergistic effect of the FeNx active sites distributed on the 3D microporous structure of the graphene oxide. The assembly of Fe, N active centres on nanostructured materials via HTC is also widely applied: Jiang et al. [56] applied the HTC strategy for the interfacial synthesis of Fe, N on carbon nanotubes (CNT) surface, in order to investigate the origin of Fe-based active sites. Glucose, melamine and iron salts together with CNTs were mixed to assemble the Fe, N derived active sites on CNTs as conductive substrates via HTC treatment. Fe/N@C catalysts containing Fe-N_x configurations and graphene-encapsulated Fe/Fe₃C (Fe@C) nanocrystals were prepared by altering the ratio of the precursors.

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The electrocatalytic tests showed that the activity of the FeN_x sites was promoted by the neighbouring Fe@C NPs, whereas the higher content of Fe-N_x sites in the presence of Fe@C NPs lead to a higher ORR activity. Serov *et al.* reported a series of catalysts using different N-C small organic molecules to coordinate with Fe. The i) mebendazole (Fe-MBZ) ii) nicarbazin, methylimidazole and glucoril (Fe-NMG) iii) nicarbazin, methylimidazole and pipemedic Acid (Fe-NMP) were synthesised via the carbonisation of Fe(NO₃)₃ with the corresponding N-C molecules, accompanied by additional urea and carbon nanotubes. The carbonisation was performed using a modified sacrificial support method, which introduced pores into the catalysts. They found that the presence

of higher amount of surface oxides and pyridinic nitrogen is an important reason for the better performance towards ORR in alkaline electrolyte.^[57] Yi et *al.* applied a gas-gel preparation method for producing Fe/N@C nanocomposites, where Fe₃O₄ NPs were embedded in a 3D cross-linking hierarchically porous N-doped carbon (Fe₃O₄@HPNC).^[58] They concluded the absence of the Fe₃C phase, therefore the role of FeN_x could be accurately investigated. The ORR results showed that both FeN_x and pyridinic N could efficiently improve the ORR performance in alkaline media, whilst in acid electrolyte, Fe-N played a more dominant role than pyridinic N in boosting the ORR activity.



Figure 1. Schematic illustration of the preparation procedures from a) pyrolysis treatment and b) HTC. Reproduced with permission from Ref. ^[26] and ^[55]. Copyright 2019 Royal Society of Chemistry and John Wiley and Sons.

Apart from the commonly reported heteroatom doped iron catalysts, the use of iron oxide NPs in ORR catalysts has also been reported. Wu et al. synthesised a N-doped graphene aerogel with Fe₃O₄ NPs with a surface area of 110 m² g⁻¹.^[59] However, they found that most of the nitrogen was incorporated close to the iron oxide NPs, suggesting the presence of some Fe/N_x sites, which leaves the contribution to the iron oxide to the ORR electrocatalysis uncertain. More recently, mesoporous carbon containing Fe₂O₃ nanocrystals was reported by He et al.[60], templated with SBA-15. A comparison with a metal-free carbon also templated with SBA-15 as well as pure Fe₂O₃ showed the superiority of the hybrid material, which the authors attributed to the iron oxide NPs acting as active sites, while the carbon enabled a better mass transport due to is mesoporous structure. In this study, no nitrogen was incorporated, excluding the presence of any formed FeN_x sites. This suggests that Fe₂O₃ NPs could act as active sites as well.

Chemical vapor deposition of carbon nanotubes has a natural electrocatalytic advantage because it usually uses Fe as a catalyst to catalyse their growth to finally obtain Fe-containing

carbon nanotubes with high electrical conductivity. Nitrogen doping on carbon nanotubes to obtain highly efficient Fe/N@C catalyst has been widely reported.^[61–64] The Fe/N@C electrocatalysts obtained using this strategy possessed improved long-term stability especially in acid electrolyte, because the iron particles were encapsulated within the carbon nanotube, which avoids the direct contact with the electrolyte and the poisoning by-product species. Theoretical studies further demonstrated that the electron transfer from Fe NPs to the CNTs result in a decreased local work function on the CNT walls while N doping into the carbon lattice can further reduce the local work function (Figure 2).^[65]



Figure 2. a) Schematic representation of the ORR process at the surface of Fe₄@SWCNT. The grey, red, white and yellow sphere represents C, O, H, Fe, respectively. b) TEM images of Pod-Fe. c) HRTEM image of Pod-Fe with the inset showing the [110] crystal plane of the Fe particle. Reproduced with permission from Ref. ^[65] Copyright 2019 John Wiley and Sons.

Several synthetic methods for producing ORR electrocatalysts were reported, and their electrocatalytic activity and stability has also been demonstrated. Despite extensive research efforts, further enhancement of the Fe/N@C catalyst's performance is needed. The difficulties lie in the fact that the synthetic methods applied, for example, direct carbonisation or HTC of Fe, N, C precursors, typically lead to heterogeneity and an ambiguous molecular geometry/morphology.^[66] Moreover, the Fe/N@C nanoarchitectures tend to aggregate forming clusters for which the atom utilization is lower than expected. [42,67] This largely reduces the catalytic activity of Fe. Furthermore, the aggregated Fe clusters usually consists of Fe present in different oxidation states (from (0) to 3⁺), making it difficult to decouple the influence of different Fe-derived active sites and identify the specific roles of single atom active sites. Therefore, producing Fe/N@C electrocatalysts with single dispersed iron is highly desired.^[68] Inorganic/organic Fe complexes which minimize the electrostatic interaction or Fe ions and therefore isolate the Fe atoms have been utilised to prepare Fe/N@C electrocatalysts.^[69] For example metal organic framework (MOF) containing metal ions and organic ligands are promising candidates to produce single atom dispersed active sites as discussed in the next section.

2.1.2. MOFs as precursors

Lately, atomic controlled synthesis has drawn much attention, as a powerful and effective strategy to avoid active site aggregation and achieve high electrocatalytic activity. An effective approach was to use metal-organic-frameworks (MOFs) as the host for Fe and N precursors.^[70] MOFs are porous hybrid materials built up of inorganic nodes, cf. metal cations or metal oxide clusters, interconnected by organic linkers, cf. polycarboxylates or heterocycles. The inorganic and organic building blocks selfassemble into typically crystalline and highly porous superstructures. Such structures have been shown to form carbonaceous matrices doped with residual inorganic components upon pyrolysis. This strategy has been successfully applied to make FeNx single-site electrocatalysts, using Ncontaining linkers such as 2-aminoterephthalic acid,[71] dicyanoimidazole^[72] and 2-methylimidazole.^[73-76] For a more general overview of MOF as precursors to electrocatalysts, readers are invited to consult more general reviews.^[76,77]

In 2018, Jiang et al. reported precisely atomic-level controlled synthesis of Fe-N-C catalysts, where the Fe-N₄ sites atomically dispersed on the three-dimensional (3D) hierarchically porous carbon possessed adjustable mass loading (Figure 3).^[78] The atomic dispersion is realised by mixing Iron (II) phthalocyanine (FePc) with Zn²⁺ and 2-methylimidazole (MeIM) to form FePcx@ZIF-8 nanocomposites (x refers to the mass of FePc added). The FePc were therefore encapsulated into the cavities of the zeolitic imidazolate framework (ZIF) during the assembly process (FePc-x@ZIF-8). The atomically dispersed FeNC catalyst was then obtained via following pyrolysis and washing. This atomic controlled strategy delivered a superior ORR activity with halfwave potential reaching 0.915 V (vs RHE) in alkaline medium, due to high atom utilisation efficiency. Their study concluded that the selective C-N bond cleavage adjacent to Fe centre could form edge-hosted Fe-N4 moieties and therefore lower the overall oxygen reduction reaction barriers. In the same year, Kumar et al. applied a similar strategy by pyrolysing ZIF-8, metal (Fe/Co)acetate and phenanthroline and studied the degradation mechanisms of the metal-NC catalysts. They found out that the FeN_x centres were more stable in acidic medium than the Fe in Fe/N@C NPs.

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Figure 3. a) Schematic illustration. b) TEM images of FePc-20@ZIF-8 composite. c) HRTEM, d) HAADF-STEM of Fe SAs-N/C-20 catalyst. Reproduced with permission from Ref. ^[78] Copyright 2019 American Chemical Society

Zhu and co-workers synthesised atomically dispersed Fe-N doped hierarchical porous graphitic carbon derived from NH₂-MIL-101 using both the linker and dicyandiamide as N source and added FeCl₃ (Figure 4).^[71] The resulting Fe/N@C electrocatalyst showed ORR activity similar to commercial Pt/C catalysts, displaying high 19.5 mA cm⁻² at -0.45 V kinetic-limiting current density, which is even higher than that of Pt/C (16.6 mA cm⁻²).



Figure 4. Preparation of NH2-MIL-101 from dicyandiamide and FeCl₃, and electrocatalytic performance. Reproduced with permission from ^[71]. Copyright 2019 American Chemical Society

Other groups took advantage of the high N content of 2methylimidazole, a building block of the ZIF-8 framework,^[79] which has also been shown to lend itself to facile heteroatom doping, a hierarchical porosity and a high degree of graphitisation on carbonisation. Wu et *al.* achieved a uniform distribution of Fe in the derived carbonaceous material by post-synthetically substituting some of the Zn²⁺ ions of the ZIF-8 framework by Fe²⁺, prior to pyrolysis. The so-obtained Fe/N@C electrocatalyst exhibited improved ORR activity with a very high half-wave potential (0.82 V vs. RHE) and sufficient potential cycling stability in acidic conditions.^[73] Deng and co-workers introduced Fe³⁺ in the ZIF-8 synthesis mixture to achieve the preservation of the ZIF-8 crystallites' shape post carbonisation at 900 °C. They found that the Fe doping greatly enhanced the fractions of graphitic-N and pyridinic-N and decreased the oxidised N fraction, resulting in 4-electron ORR catalysts that were much more stable than commercial Pt/C electrocatalysts in acidic media.^[74]

An alternative approach was employed by Lai *et al.* They introduced a Fe-methylimidazole nanocluster inside the ZIF-8 pores before pyrolysis, which was then transformed into Fe-N/C electrocatalysts with controllable structures (Figure 5). The subsequent host-guest interactions resulted in different types of FeN_x sites (x = 2 to 5) on the porous carbon matrix. Their combined experimental-theoretical scrutiny revealed that pentacoordinated FeN₅ sites significantly promoted the ORR reaction rate in acid media, due to the small energy barrier and the low adsorption energy of intermediate OH on these sites.^[75]



Figure 5. FeN₅@C made from ZIF-8, application to ORR. Reproduced from ^[75]. Copyright 2019 American Chemical Society

The utilisation of ZIF-8 for the preparation of Fe/N@C electrocatalysts was further expanded by Ye *et al.* who found that a pre-heating step of the Fe-ZIF-8 precursor (200°C) before carbonisation (800°C) was key in boosting the coordination between the doped Fe and N-containing ligands (Figure 6). Their optimised catalysts reached ORR catalytic performance with a half-wave potential of 0.88 V and limiting current density of 6.0 mA cm–2 in 0.1 M KOH.^[80]

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Li *et al.* designed a special lamellar MOF, DCI-Fe, based on Nrich dicyanoimidazole and Fe(OAc)₂, which yielded Fe/N@C without the need to further add N or Fe-dopants. The resultant Fe/N@C electrocatalysts exhibited superior stability and activity to commercially available Pt/C ORR catalysts in alkaline media.^[72]

Figure	6.	Two-st	teps	synthe	sis o	f Fe	N _x @C,	ele	ctroch	emical	per	formanc	e.
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Reference	Sample Name	Synthesis method	Precursor	Electrolyte	Onset potential of catalyst [mV vs RHE]	Onset potential of Pt- C standard [mV vs RHE]	Limiting current of catalyst at 0.6 V vs RHE [mA cm ⁻²]	Limiting current of Pt at 0.6 V vs RHE [mA cm ⁻²]
[26]	Fe/N/CNT@P CF	pyrolysis	Catkins, Melamine, FeCl ₃	0.1 M KOH	879	892	4.1	4.6
[48]	N-CNF aerogel	pyrolysis	Bacterial cellulose	0.5 M H ₂ SO ₄	830	900	2.1	2.1
[54]	Fe/N-CNFs	HTC+pyrolysis	d(+) - glucosamine hydrochloride and ferrous gluconate	0.1 М КОН	880	950	5.6*	5.5*
[55]	Fe _x N/NGA	HTC+pyrolysis (NH₃)	Graphene, iron phthalocyani ne	0.1 М КОН	947*	-20*	5.5*	5.2*
[56]	Fe@C-FeNC- 2	HTC+pyrolysis	Glucose, CNT, melamine, Fe(NO ₃) ₃	0.1 M KOH	980*	960*	5.2*	5.4*
[60]	OMCs-Fe ₂ O ₃	Vacuum calcination (350 °C)	Sucrose, Fe(NO ₃) ₃	0.1 M KOH	910	940*	3.9	5.1*

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[78]	Fe SAs-N/C- 20	Atomic-level control	ZIF, iron (II) phthalocyani ne (FePc)	0.1 M KOH	970*	920*	6.1*	5.5*
[71]	Fe/N-GPC	Pyrolysis, then acid etching	MIL-101-NH ₂ MOF	0.1 M KOH	1015	985	4.8*	4.8*
[73]	C-Fe-Z8-Ar	Pyrolysis(1000 °C, 1h)	ZIF-8	0.1 M HCIO4	950	990*	7.1*	5.8*
[74]	C-FeZIF-900- 0.84	Pyrolysis (900°C, 3 h) then acid etching	ZIF-8	0.1 M KOH	950	990*	7.0*	5.2*
[75]	5% Fe-N/C	Two-step pyrolysis, then acidic treatment	ZIF-8	0.1 M HCIO₄	861	1018	4.8*	5.8*

[80]	Fe-N/C	Two-step pyrolysis	ZIF-8	0.1 М КОН	850*	950*	6.0	5.5*
[72]	DCI-Fe-700	Calcination (700°C)	DCI MOF	0.1 M KOH	1030*	1030*	6.0*	6.2*
* Values estimat	ted from LSV grap	hs (unless otherwi	se noted at 1600 i	rom). Potentials w	ere converted as f	ollows: ERHE = EAG		591xpH

Table 1. Summary of each presented reference for ORR.

2.2. Fe/N@C in CO₂RR

CO₂ reduction via electrochemical routes (CO₂RR) has attracted much attention recently, as an alternative and intermediate solution to energy generated entirely based on renewables. CO₂ emitted from the use of fossil fuels can be captured and converged back into fuels into a circular economy fashion.[81] Different electrocatalysts have been used for CO₂RR, mostly based on noble metals (Ag, Au, Pd). There are different challenges for this process, such as the need of high overpotentials for the formation of hydrocarbons, a complex process that requires numerous electron transfers as well as going through many intermediate species. Due to the required overpotential, different reactions can take place in the cathode, depending on the catalyst and reaction conditions, amongst which the hydrogen evolution reaction (HER) will lead to the formation of H₂ which will be present along with the CO₂ electroreduction products.^[82] The main objective for this process consists in finding inexpensive, selective and stable catalysts, operating at low overpotentials.^[7] Based on this goal, a lot of research has been devoted to transition metals and N co-doped carbon catalysts (M-N-C). The advantage of doping transition metals and N into the carbon matrix, consists in changing the neutrality and increase charge and spin densities, going from an inert carbon to an active electrocatalyst. Porphyrin-type macrocycles showed good reactivity towards CO₂ reduction to CO both as homogeneous and heterogenous catalysts, but they possess poor stability. The possibility of using these M/N@C porphyrin-type catalysts for CO2RR, was first reported by Varela et al.[83], proving that this class of carbon-based materials represent a cost-effective alternative to carbon-supported Au catalysts for CO₂RR to CO/H₂ mixtures. The overall electrocatalytic performance of Fe/N@C was evaluated by linear sweep voltammetry (LSV), showing a clear improvement in the catalytic activity of CO2RR after incorporating metal ions into porphyrin. Further investigation was performed via stationary bulk electrolysis and stationary product

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selectivity at a constant electrode potential, using gold catalysts as a benchmark. The results pointed out a sharp increase of the stationary CO₂ reduction with the Fe incorporation, confirming that the catalyst is selective for the production of H₂ and CO via 2electron transfer reaction. By shifting the potentials towards more negative values (~ -0.8 V_{RHE}) the formation of CH₄ has been detected, correlated with M-CO interaction strength, as the formation of this hydrocarbon on Fe-N-C moieties takes place at 0.93 V overpotential (-0.76 V_{RHE}).^[84] Huan et al. ^[85] worked on the influence of the structural parameters of Fe/N@C on the CO2RR selectivity. They synthesised five different Fe/N@C catalysts varying the single-Fe-atom centres, Fe-containing NPs and metal loading (from 0 to 4 wt% Fe). By pyrolysing Fe_{0.5}d in NH₃, characteristic signals of crystalline Fe₂N and Fe_{2+x}N were identified. Also, Fe was present as atomically dispersed ions in the N-doped carbon matrix as square-planar Fe^{II}N₄ and Fe^{III}N₄ species in low- and medium-spin state. Other Fe containing species were α -Fe, iron carbide Fe_xC and γ -Fe, and it was observed that the formation of crystalline Fe structures decreased by decreasing the Fe content. During catalytic tests, the materials have been grouped in two classes, based on their onset potential. Regarding the reduction products, CO and H₂ were the main products. In this way the materials possessing a high fraction of Fe in the form FeN₄ moieties present high selectivity for CO with faradaic yield (FY) up to 80% at -0.5V vs RHE. Similar observation was obtained by Ju et al. [86], who reported 65% FY for CO at -0.55V vs RHE. Fe in the form of crystalline Fe produces high FY for H₂ at all potentials. Along with CO and H₂, traces of CH₄ have been detected, the highest FY being 1.5% at -1.0V vs RHE. Overall, according to Huan el al. [85] the amount of FeN4 moieties determines the CO formation relative to H₂ evolution. Regarding H₂ formation, it is still under the question of whether all or just specific Fe-based crystalline structures are responsible for it. Further investigations on Fe/N@C for CO2RR have been carried out by Yang et al. [87] Based on previous work on oxygen reduction reactions (ORR) using Fe/N co-doped carbon materials as catalysts, they proposed a comparative study on ORR and CO₂RR using Fe/N@C catalysts prepared by pyrolysis and further oxidation at 80°C, 160°C and 240°C. When tested in CO2RR it has been observed that the higher the oxidation temperature, the larger the reduction current at high overpotentials. In this way, the FY for CO was slightly improved from 78% at -0.64V for the unoxidised samples, up to 86.7% for the high temperature oxidised samples. The negative side of the oxidation process is that a high temperature might result in collapsing the active sites, as they reported a small decrease of the CO FY for the catalysts treated at 240°C. Despite the improvements the oxidation step showed towards CO₂RR, ORR seems to be negatively affected after oxidation is applied. This may be because during the oxidation the content of graphitic N, which has been reported as being the active site for ORR, is decreasing.^[88] Overall, they found out that CO2RR and ORR occurred over different Fe/N@C active sites. Pan *et al* ^[89] reported positive catalytic activity for Fe/N@C catalysts towards CO₂RR, with FY more than 98%. The main products were CO and H₂ with small traces of CH₄. A comparison between N-C catalysts and Fe/N@C for CO₂RR can be made as flowing. On N-C the reduction starts at -0.60 V, the CO FY is about 50%, reaching a maximum of 78% at -0.89 V which means 0.78V of overpotential; on Fe/N@C CO₂RR starts at -0.30V with CO FY of 53%, increasing up to 87% at an overpotential of 0.38 V (Figure 7a). Moreover, CO current densities for Fe/N@C electrode are larger than those of N-C at the same potentials (Figure 7b).



Figure 7. a) Faradaic efficiencies and b) Partial current densities for CO and H_2 of N-C and Fe-N-C at different applied potentials in CO₂-saturated 0.1 M KHCO₃ Reproduced with permission from ^[89]. Copyright 2018 Elsevier

The role of Fe was further investigated by poisoning the Fe-N coordination sites with SCN⁻ ions. During the CO₂RR in the presence of KSCN, the selectivity for CO was about 25% smaller than KSCN-free experiments, reaching a maximum of 62% at - 0.59V. Also, the CO currents decreased when the H₂ Faradaic efficiency (FE) increased, underlining the importance of Fe for the CO₂RR.

Hu et al. [73] synthesised nitrogen and metal (Fe, Co and Ni) codoped electrocatalyst via hard templated method, using SiO₂ as sacrificial template. When tested in CO2RR, Fe/N@C performed different according to the synthesis procedure. Without removing the SiO₂ template, the FE for CO was very low (11% at -0.57 V vs RHE). The FE was increased to 58% after template removal and increased even further to 81% (-0.57V vs RHE) after a second pyrolysis step. In this step, the oxygen functionalities gained during template etching had been removed. In order to confirm the importance of the porosity, Fe/N@C have been synthesised without any template. As a result, the CO FE decreased up to 66% and the current density decreased as well. Another parameter that has been modified was the electrode potential. They managed to obtain CO FE of 70% at -0.37V vs RHE, which represents a very low overpotential considering the equilibrium potential for CO2-to-CO conversion (-0.11v vs RHE).

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Ref.	Sample Name	Synthesis Method	Precursor	Electrolyte	CO FE %	Overpotential*
						(mV)
[89]	Fe-N-C	Solid phase pyrolysis	Urea	0.1M	87	380
			Citric acid	KHCO ₃		
			Fe(NO ₃) ₃			
[87]	Fe/N/C	Carbon black coating	Phenylenediamine	0.1M	87	646
		and acid treatment	(NH ₄) ₂ S ₂ O ₂	Narico3		
			KJ600 carbon black			
			FeCl₃			
[85]	Eo N C	2 Stop pyrolycic	715 9	0.1M	01	490
	1 6-14-0		211-0	NaHCO ₃	51	490
			Fe(C ₂ H ₃ O ₂) ₂			
			Phenanthroline			
[83]	Fe-N-C	Consecutive	FeCl3	0.1M	80	390
		etching	Polyaniline	KHCO3		
			Ketjenblack carbon			
[90]	Fe-N-C	Silica templated	o-Phenylene diamine	0.5M	85	360
		pyrolisis	FeCl₃	KHCO₃		
			Colloidal Silica			
[86]	Fe-N-C	Carbonisation	4,4'-Dipyridyl hydrate	0.1M	65	440
		followed by impregnation	FeCh	KHCO₃		
			10013			
[91]	Fe-N-C	Thermal activation	Fe-doped ZIF8	0.1M KHCO₃	93	470
			Zn rich MOF			
[89]	N-C	Solid phase pyrolysis	Urea	0.1M	78	780
			Citric acid	KHCO3		
[10]	Au nanoparticles	Precipitation	HAuCl ₄	0.5M	90	560
	- 1 A		Tetralin	KHCO3		
[92]	Pd nanoparticles	Reduction-	NaBH ₄	0.1M	91	780
		Stabilization	Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O	KHCO3		
			PdCl2			
*Overpotent	ial at which the maximum	FE is achieved				
-						

Table 2. Summary of Fe-N-C catalysts for CO₂RR.

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2.3. Summary

Overall, the synthesis of electrocatalysts with abundant active sites and superior ORR catalytic activity has developed a lot during the past few years and has proved Fe/N@C to be a very promising electrocatalyst to replace the Pt from fuel cells. Yet, fundamental studies are still needed to understand the mechanisms of the active sites. Atomically-controlled synthesis assisted by MOF has demonstrated superior catalytic activity and obviously better-defined atom-coordination for fundamental study comparing with the traditional methods such as HTC and pyrolysis methods. However, their delicate and complicated syntheses remain an impediment for their widespread application in industry. Furthermore, Fe/-N@C electrocatalysts have gained a lot of space in the CO₂RR.^[83–85] Representing a green and cheap alternative to the noble metal based electrocatalysts^[93] and owing their improved catalytic activity and selectivity, in contrast to metal-free N-doped carbon materials, they represent an obvious choice when it comes to high FE for CO at low overpotentials. Tables 1 and 2 gather together recent results for ORR and CO₂RR on Fe-N-C catalysts.

3. Fe/N@C heterogenous catalysts in organic chemistry

3.1. NO₂ and C=N reduction

The first reaction explored using Fe/N@C catalysts was nitroarene reduction. Anilines are crucial intermediates in the dye industry and polyurethane manufacturing.^[94] They are industrially produced from nitrobenzene hydrogenation, based on heterogeneous Pt, Pd or Cu at 200-300°C under H₂ gas (1-10 bar).^[95] Switching to milder hydrogenation conditions and catalysts with abundant metals is thus imperative, considering that world consumption of aniline is expected to grow at 5% per year for the next 5 years.^[96]

In a seminal report in 2013, the Beller group reported a new heterogeneous catalyst for this reaction based on Fe supported on carbon.^[97,98] They made their catalyst by pyrolysing at 800°C a pre-formed Fe-phenantroline complex deposited on Vulcan XC72R (Fe-phen/C-800, Scheme 1). Throughout this paper and every subsequent report of the Beller group, the phenantroline precursor consistently gave the best catalytic results. In only one example (covered below), an N-aryliminopyridine (labelled as aminopyr on Scheme 1) has been proved to provide a 4-fold higher activity for N-heterocycle hydrogenation.^[99]



Scheme 1. Synthesis of Fe-phen/C-800 and Fe-aminopyr/C-800.

Fe-phen/C-800 was tested towards nitroarene hydrogenation into anilines, over a range of 39 substrates, and afforded high yields ranging from 86 to 97% (Scheme 2). Nitroarene transfer hydrogenation using HCO₂H-Et₃N was also successful, with 87-95% yields.^[98] Notably in both cases, the reaction showed a remarkable chemoselectivity, leaving C=O, C≡N, C=N, C=C and C-X (X = S, F, Cl, Br) bonds untouched. Authors also performed *in situ* alkylation of the resulting aniline in the presence of an aldehyde with yields in the 46-94% range (28 examples).^[100] Using paraformaldehyde, the authors extended their scope to tertiary amines, in the form of N,N-dimethylanilines.^[101] Under reaction conditions, paraformaldehyde depolymerizes into formaldehyde, then decomposes to H₂ and CO thus providing *in situ* both C1 source and reducing agents. In all cases the catalyst was recyclable up to 5 cycles and performed well on the 1-10 g scale. Lastly, the authors showed that the catalyst could also be used under water-gas shift conditions (CO + H₂O).^[102]

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By replacing the phenantroline ligand with an N-aryliminopyridine ligand, the authors tuned their catalyst properties to make them efficient in the quinoline derivative hydrogenation (64-98% yield, 31 examples).^[99]

Since Beller's initial discovery, other groups developed their own approach to produce Fe/N@C based on different. Zhang et *al.* made N-doped graphene oxide (rGO-N) through a modified Hummers method, using a KMnO₄/NaNO₃/H₂SO₄ mixture to oxidize graphene. rGO-N was then impregnated with Fe(OAc)₂ and pyrolyzed at 800°C.^[103] The BET surface area was about 3.5 times higher compared to Fe-phen/C-800 (358 m²g⁻¹ instead of 100 m²g⁻¹), allowing milder conditions for nitroarene hydrogenation (30 bar H₂, 100°C instead of 50 bar H₂, 120°C). However, the yield dropped by 10-20 %-points upon each recycling. Bäumler *et al.* opted for a slightly different approach, using siliconcarbonitrite (SiCN) as a N-containing support instead of a pure carbon based support.^[104] The catalyst was competent for *in situ* alkylation of the resulting aniline in the presence of an aldehyde (62-92% yield, 17 examples). In their case though, they extended the concept to diketones to allow the synthesis of quinoxalines and benzimidazoles (75-95% yield, 6 examples).

3.2. C=O bond reduction

Despite the better reactivity of Fe/N@C towards nitroarene reduction (see previous section), C=O bond reduction shines a primary goal in biomass catalytic conversion.^[105] Indeed, the oxygen content of biomass-derived substrates is usually higher (30-50 wt% in lignocellulosic biomass) than in fossil fuel. As this is amount is usually higher than in the desired product chemicals, deoxygenative and reductive processes are key reactions in the biomass conversion industry.

The Fu group re-purposed the Fe-phen/C-800 catalyst developed by the Beller group towards C=O reduction, with a focus on biomassderived substrates. First, they explored the transfer hydrogenation of furfural into furfuryl alcohol (Scheme 3A).^[106] Using *sec*-butanol as a reductant and solvent, their optimised conditions (160 °C, 15 h) gave 83% selectivity and 92% conversion of the starting material. Then, they explored 5-HMF deoxygenation into dimethylfuran (DMF), using both H₂ and *n*-butanol as reductants (Scheme 3A).^[107] In both cases catalyst recyclability was excellent (5 cycles) and 5-HMF deoxygenation could be transposed to continuous-flow synthesis, with a consistent DMF yield above 80% over 72 hours. The catalyst has been applied as well to the hydrogenolysis of C-O bonds in lignin model compounds (Scheme 5C).^[108] Over 15 different β -O-4 and α -O-4 (benzyl phenyl ether) model compounds, Fe-phen/C-800 afforded a mixture of aromatics, leaving the aromatic rings untouched. This feature is particularly interesting since noble metals are prone to arene hydrogenation.

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Scheme 3. Fe-phen/C-800 applied to biomass hydrogenation and hydrogenolysis of: A) Furfural B) 5-HMF C) Lignin model compounds.

At the same time, the Fu group explored another Fe/N@C synthetic pathway, through the pyrolysis of Fe(acac)₃ over graphitic carbon nitride, made from melamine, and activated carbon at 900°C.^[109] Subsequently, a HCl treatment was employed to dissolve agglomerated and unprotected Fe_xO_y nanoparticles (NPs) and increased the catalyst stability. An optimal Fe loading of 20% on the support afforded a high yield of 86% for 5-hydroxymethylfurfural deoxygenation to dimethylfuran, at shorter reaction times but higher catalyst loadings than with Fe-phen/C-800 (2 h, 60 mol% Fe instead of 12 h, 11 mol% Fe).

3.3. C-N and C-O oxidation

Oxidative processes using Fe-phen/C-800 were tackled as well, most notably dehydrogenation of amines, alcohols and N-heterocycles. Nitriles are important building blocks for conductive organic polymers, as well as pharmaceutical targets.^[110] At the laboratory scale, the classic synthetic pathway involves the reaction of metal cyanides or HCN with organic halides. Yet the high toxicity of these reagents makes them unsustainable on bigger scales. In 2000, a cyanide spill in Baia Mare, Romania resulted in the worst environmental disaster in Europe since the Chernobyl disaster.^[111] Ammonoxidation via the Sohio process is the preferred industrial pathway in industry to access nitriles, using O_2 and NH₃ to convert methyl groups into -CN groups.^[112] On the plant scale, Bi-MoO catalysts are used at 470 °C for the production of acrylonitrile.^[113] Yet, owing to the harsh condition of ammonoxidation conditions, this process cannot be generalised beyond parent compounds. The Beller group showed that Fe-phen/C-800 could oxidise primary alcohols or primary amines to nitriles using O_2 (Scheme 4).^[114,115] The presence of aqueous NH₃ helped quench the formation of secondary imines. The catalyst gave 82-97% yield over 63 examples, even at gram-scale oxidation for 4 amines. In a similar protocol, Murugesan et *al.* adapted the catalyst to aldehyde conversion to nitrile in presence of aqueous NH₃, under milder conditions (40°C, 1 bar O_2).^[116] The system was proved to be active over a wide range of heterocyclic aldehydes, as well as aliphatic aldehydes (86-96% yield, 52 examples). By switching the solvent to H₂O, the resulting nitrile can be further hydrolysed to amides (70-90% yield, 15 examples).

1				
	R XH X = O, NH	aq. NH ₃ (6 equiv.), O ₂ (3 bar)		82-97% vield
	Fe-phen/C-800	<i>t</i> -amyl alcohol, 110-150°C, 15h		(63 examples)
į	(4 mol% Fe)		R—≡N	
		aq. <mark>NH₃</mark> (6-10 equiv.), <mark>O</mark> 2 (1 bar)	1	86-96% yield (52 examples)
	R [∕] ≷O	<i>t</i> -amyl alcohol, 40°C, 24h		(of examples)
	Fe-phen/C-800	aq. NH ₃ (3 equiv.), air (10 bar)		70-90% yield
i	(3-5 mol% Fe)	H ₂ O, 120°C, 24h		(15 examples)

Scheme 4. Fe-phen/C-800 applied to nitriles and amides synthesis under oxidative conditions.

Alcohol and N-heterocycle dehydrogenation serve multiple purposes.^[117] Unlike oxidation, dehydrogenation reactions are conducted under inert atmosphere, liberating H₂ in the process. In cases where reverse hydrogenation is possible, substrates such as N-

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heterocycles can be used as liquid H₂ storage medium.^[118,119] Alcohol dehydrogenation generates carbonyls along with H₂ gas, that are reactive intermediates. Primary alcohol dehydrogenation into aldehydes is of interest, as the absence of O₂ prevents its overoxidation to carboxylic acid. These carbonyls can be further used in tandem reactions, and condensed *in situ* with amines, indoles, or other alcohols.^[120] State-of-the-art catalysts are homogeneous Rh, Ru and Ir complexes,^[121,122] although current efforts are focused towards base metals and heterogeneous catalysts (and ideally both).^[123,124]

Balaraman *et al.* explored dehydrogenative processes using Fe/N@C, supported on exfoliated graphene oxide this time (Fephen@EGO-900, Scheme 5A).^[125] Fe-phen@EGO-900 was first tested on N-heterocycle dehydrogenation, using 10 mol% *t*BuOK at 145 °C under Ar, with the release of H₂ gas (33-94% yield, 20 examples, Scheme 5B). It was then tested for alcohol dehydrogenation, successfully generating the corresponding carbonyl in moderate to good yields (31 examples). Then, the authors tested their catalyst for primary amine oxidation to form symmetric secondary imines (49-96% yield, 8 examples). The system was further adapted to alcohol and amine dehydrogenation-condensation tandem sequence towards non-symmetric secondary imines (33-94% yield).^[126]



Scheme 5. Fe-phen@EGO-900 A) Synthesis B) Dehydrogenative applications.

Yang *et al.* prepared Fe₂O₃ NPs supported on N-doped graphene nanosheets, through the HTC of urea, graphene oxide and FeCl₃ (NG-Fe₂O₃).^[127] The authors used the catalyst for the oxidation of a range of benzaldehyde derivatives into the corresponding carboxylic acid, using O₂ or *tert*-butyl hydroperoxide as an oxidant (40-99% yield, 21 examples). To maximize the amount of FeN_x single site, Zhang et *al.* deposited FeCl₃ and *m*-phenylenediamine onto a porous carbon support (Ketjen Black EC-600JD), that was subsequently oxidised using (NH₄)₂S₂O₈ and pyrolyzed at 900°C, 1h.^[128] The catalyst was successfully applied to alcohol oxidation to aldehydes under O₂ (5 bar, 64-100% yield, 5 examples).

3.4. C-H oxidation

FeN_x are the active sites of metalloporphyrins contained in cytochromes P450 enzymes. They are widely used in the biological world for the highly regioselective and chemoselective oxidation of $C(sp^3)$ -H and $C(sp^2)$ -H bonds.^[129] Converting C-H bond into C-OH functionalities is a powerful tool for both late-stage functionalization in total synthesis,^[130] but also for upstream functionalization of unsaturated substrates. For instance, the vast majority of cyclohexanone and cyclohexanol is industrially produced from cyclohexane oxidation under air, using Co as a catalyst.^[131] The two examples reported so far consisted in atomically dispersed FeN_x sites over the carbon support, constituting ideal study models for active site identification. A more thorough description of their respective studies is provided in the last section. Deng et *al.* milled iron phthalocyanine (FePc) over graphene nanosheets, resulting in a FeN₄@C material, and used it for benzene conversion to phenol using hydrogen peroxide.^[132] Liu et *al.* opted for the deposition of Fe(phen)₃ complexes on a nano MgO template, followed by pyrolysis (600-900 °C, 2 h) of the material (FeN_x@C, x = 4-6) and dissolution of MgO using

HNO₃.^[133] The catalyst was tested for the oxidation of hydrocarbons in water, using *tert*-butyl hydrogen peroxide as an oxidant (62-99%) yield, 9 examples).

3.5. Summary

After only 6 years of development of Fe/N@C catalysts in organic reactions, a wide array of processes has already been covered (

Table).^[134] Initiated by Beller's initial discovery, nitroarene hydrogenation and reductive amination pathways have been widely explored based on their Fe/phenantroline system. Fu et *al*. furthered the field by applying the same catalyst onto bio-based substrate C=O hydrogenation/deoxygenation. Finally, oxidative pathways were developed by Jagadeesh et *al*. on nitrile synthesis,

and Balaraman *et al.* on alcohol and N-heterocycle dehydrogenation. Similar materials containing atomically dispersed FeN_x centres on carbon were tested on a few C-H oxidation examples. The applications of Fe/N@C in organic chemistry are already diverse, with a range of industrially relevant processes.

Substrate	Reaction	Conditions	Product	Reference	
		H ₂ (50-65 bar)			
	Reduction	or HCO2H/NEt3 (3.5 equiv.)	R^{-NH_2}	[97,98,102,104]	
_ < NO ₂		120 °C, 12-24 h			
R -		(CH ₂ O) _n (20 equiv.)			
	Reductive alkylation	or R'-CHO/H ₂ (60-70 bar)	н R ^{´N} `R'	[101,104]	
		120-170 °C, 20-48 h			
		H ₂ (40-50 bar)		[99]	
N		130-150 °C, 60-72 h	N		
_	Reduction				
0		sBuOH	ОН	[106]	
止0		160 °C, 15 h	≌0		
НО		H₂ (40 bar), <i>n</i> BuOH		[107]	
0	Dooxygonation	240 °C, 12 h	0		
	Dooxygenation	H ₂ (10 bar)			
Lignin		240 °C, 12 h	Phenols	[108]	
R ^{NH} 2		NH ₃ (aq., 5-10 equiv.),		[114]	
R ^A O	Ammonoxidation	O₂ (1-3 bar)/air (10 bar)	R─≡N	[116]	
i o	× *	40-150 °C, 24 h			
ROH				[115]	
IX OIT	Dehydrogenation	<i>t</i>BuOK (10 mol%)	$R \sim O + H_2$	[125]	

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Table 3. Reactions catalysed by Fe/N@C.

4. Identification of FeN_x single sites

Understanding the nature of the active sites is crucial for the development of FeN_x-containing catalysts. Whether the active site is a single catalytic site or lies at the Fe/N interface, its identification on a carbon support is highly challenging. In this section, we first describe the techniques typically reported towards FeN_x centres characterisation, as well as list some techniques that have not been applied yet to this field, in an effort to foster future progress. Then, we explored the application of these various techniques in the context of each catalysis for insightful study of the catalysis mechanism.

4.1. Advanced characterisation of FeN_x single site (SSC) catalysts

X-ray absorption spectroscopy (XAS) allows very specific probing of the species of interest by selectively exciting core electron or nuclear transitions of unique energy. Their limited application is the result of the necessity of using high intensity monochromatic radiation at desired frequencies, i.e. it is desirable that the energy may be varied to access different elements and different shells. The availability of such techniques is often restricted to synchrotron facilities. Additionally, with improved time resolution and novel developments of in situ and in operando sample environments, there has been an increasing number of studies focused at the understanding of the functioning of catalysts under relevant operating conditions. Whilst most of these studies are still aimed at precious metal catalysts, there are now examples of their application to the study of single-site Fe catalysts. In the following section, we will briefly review the various techniques and give examples on their application to explore the operation of FeN_x single site catalysts. As there are excellent review papers focused on the individual techniques, we will focus below on highlighting the types of information one may extract from a given methodology and will provide the reader with references to more comprehensive review papers on the individual techniques.

X-ray absorption near-edge structure (XANES) In spectroscopy, the absorption of a photon results in the excitation of an electron from a core state to an empty state. For this excitation to take place, the photon energy has to equal or surpass the binding energy of this core-level. As the photon energy is scanned, this opens a new absorption channel. The energy of an absorption edge therefore corresponds to the corelevel energy, which is characteristic for each element. The spectral shape in the near-edge region is determined by the electronic density of states and thus mainly yields information on the electronic properties, such as oxidation state, and to some degree of the local geometry of the absorbing atom.[119] At the higher end of the energies in the XANES region, the extended Xray absorption fine structure (EXAFS) region is found. In contrast with the former, the EXAFS region is dominated by the outgoing electron single-scattering events on the neighbouring atoms. Therefore, this technique is a sensitive tool of the local geometry of the microenvironment surrounding the absorbing site. For further reading on XANES and EXAFS the reader is invited to consult the following excellent review papers and books.[135-139]

XAS proved to be a powerful tool for the in operando study of FeOOH supported on N and O-doped carbon, applied to CO_2 electro-reduction into acetic acid.^[140] The N-dopants on carbon have been shown to stabilize the Fe(II) active species against reduction to Fe(0) ($E^0(Fe^{2+/}Fe^0) = -0.64 \vee vs Ag/AgCI$) in the CO_2RR selective potential region (Figure 8a), whereas O-doped carbon did not provide such as stabilising effect (**Fehler! Verweisquelle konnte nicht gefunden werden.**). In operando Fourier-transformed EXAFS investigations in the course of

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electrode polarisation also suggested that the HER activity is concomitant to the rapid switch between the reduced Fe(0) and oxidised Fe(ii), suggestive of a reaction mechanism in which the oxidation of intermediate hydride species to H₂ is accompanied by the reduction of Fe²⁺ to Fe⁰.



Figure 8. FY-mode Fe K edge XANES spectra measured in quick mode in 0.05M KHCO₃ at different potential and corresponding EXAFS spectra (inset) for the Fe/N-C. a CO₂RR selective region and b HER selective region. Reproduced with permission from ^[140], Copyright 2018 Nature Publishing Group

In Deng's report, FePc complexes were dispersed over graphene by ball-milling.^[132] By Fourier transformation of the EXAFS signal of their material, the authors determined the environment around Fe. Typically, the absence of Fe-Fe bonds was useful in proving the atomic nature of Fe.

In heterogeneous catalysis the chemical state of surface species is of paramount importance and X-ray photoelectron spectroscopy (XPS) has always been extensively used to characterise catalyst surfaces. However, it has severe limitations, particularly in the softer energy range of X-rays as it necessitates the probing of the sample in ultra-high vacuum (UHV), failing to emulate real-life conditions. The scattering of photoelectrons by gas molecules can be overcome by limiting the distance that electrons have to travel through the gas atmosphere. The electrostatic lenses, their arrangement, and efficient differential pumping need to be applied. The greatest technical challenge consists in focussing the X-ray beam onto the sample area in front of the aperture, without beam obstruction by the aperture itself. Furthermore, synchrotron sources have the advantage that they provide more tightly-focussed beams with high flux and smaller divergence than lab sources. This has allowed the development of ambient-pressure XPS (APXPS) instrumentations.[141] Synchrotron-based APXPS further allows for the modulation of the excitation wavelength, which in turn may refine the penetration depth of the probing beam.^[141,142] Using a combined APXPS and theoretical approach, Artyushkova et al. found that oxygen binds to the N atoms in Fe–N–C ORR electrocatalysts and that it is the nitrogen and bound-oxygen with the adjacent Fe atom that leads to the enhanced activity favouring the complete ORR seen for FeNC electrocatalysts.^[143] Genovese et *al.* also used XPS to demonstrate that the preferential Fe-binding site is on the pyridinic N species on a N-doped carbon sample, which site is also more prone to reduction to the active Fe(ii) species when exposed to 0.15 mbar H₂O.^[120]

Nuclear resonance fluorescence spectroscopy, or Mössbauer spectroscopy, is based on the recoil-free emission and absorption of gamma rays in solids. It provides very sensitive information on the nucleus's electronic state, and magnetic and coordination structures through hyperfine interactions. ⁵⁷Fe Mössbauer spectroscopy provides information on the chemical nature of all distinct Fe microenvironments within a sample, including oxidation and spin state, symmetry of the Fe coordination sphere, nuclearity of a cluster with more than one metal ions, electron spin ground state of the cluster, and delocalisation properties in mixed-valent clusters. Furthermore, the technique allows for a quantitative analysis. However, it is restricted to samples in the solid state and it is also poorly adaptable to follow quick changes in the specimen.^[144,145] In Deng's example, where atomic sites FeN_x sites were dispersed over graphene by ball-milling (FeN₄/GN-2.7), ⁵⁷Fe Mössbauer was particularly useful in identifying the active site. [132] Mössbauer spectroscopy is also one of the best tools to call upon when EPR inactive low-spin Fe(ii) complexes are of relevance, which is a relatively common occurrence in the case of FeN_x single-site catalysts on account of the soft acid character of many of the Nbearing functionalities resulting in small crystal field splitting, as also observed by Liu and co-workers.[133]

Nuclear forward scattering (NFS, also known as nuclear resonance vibrational spectroscopy, NRVS or nuclear inelastic scattering, NIS) is a synchrotron radiation-based method that extends the energy range of conventional Mössbauer spectroscopy to the range of molecular vibrations, it therefore reveals the full spectrum of vibrational dynamics for Mössbauer nuclei. ^[146] In addition, as in the case of NFS all spectral lines are excited concomitantly, taking advantage of the white, broad spectrum, synchrotron radiation, it is a much better suited methodology for operando studies as it allows for time-dependent investigations as long as the Fe-species life time exceeds the 1.4x10⁻⁷ s Mössbauer window.^[146] Although NRVS has not been reported so far to identify FeNx sites, it has successfully been applied to identify atomic Fe(II) sites in zeolites by Snyder et al.[147] Indeed, three different FeSI₄Al₂O₆ configurations were possible (2T6, 2T4 and 2T8), and EXAFS was not sensitive enough to resolve the distribution of AI within the active site. 2T6 had a distinct signature signal by NRVS at frequencies <250 cm⁻¹, since it missed one in-plane equatorial bending motion compared to site of their material as 2T6 sites (Figure 9).



Figure 9. Experimental NRVS spectrum of Fe(II)-BEA. Adapted from Reproduced with permission from ^[147]. Copyright 2018 National Academy of Sciences

Though strictly speaking not a materials characterisation method, increasingly sophisticated systems increasingly rely on supporting understanding of characterisation techniques by computational modelling. This is none the least relevant for catalytic reactions, including single-site catalysts, an area that has undergone a tremendous amount of progress thanks to method development, increased computational power. [148,149][150-155][152,155-^{160]} Computationally assessing catalytic activity by relating it to descriptors instead of calculating the activation energies of elementary reaction steps in heterogeneous catalytic reactions has been significantly relying on screening linear free energy relationships (LFERs), or linear scaling relations [161-163] [164,165][166-^{169]} However, the direct transposition of LFER on the single-site systems is problematic as the simple models used for bulk metal systems are not satisfactory to describe directional metal-ligand bonds. [170,171] Recently, Gani et al. were able to model Fe(ii) single-site catalyst (though not FeN_x) for methane hydroxylation, demonstrating that i) the tuning of the ligand field strength yields LFERs and ii) scaffold distortion not only breaks strong linear scaling relations arising from ligand field strength tuning but also alters BEP relations for oxo formation (Figure 10). We believe that such approach could be very helpful in rationalising reaction mechanisms on FeN_x single-site catalysts in the future.^[172]





Figure 10. Understanding and Breaking Scaling Relations in Single-Site Catalysis: Methane to Methanol Conversion by Fe^{IV}=O. Reproduced with permission from ^[172]. Copyright 2018 American Chemical Society

4.2. Atomically dispersed $\mbox{FeN}_{\mbox{x}}$ for ORR and mechanism study

Though extensive research has been carried out on these nonnoble metal catalysts with many reporting promising catalytic activity and stability, both the ORR and CO2RR mechanisms, for example, the different configuration and role of active sites, are still debated due to contradictory reports.[173] The most common concept is based on FeNx active sites incorporated into the carbon framework, similar to the metal phthalocyanines first reported by Jasinski.^[11] Proposed structures of these active sites of non-noble metal catalysts containing iron can be found in Figure 1111. Most research assumes the iron ion to be surrounded by four nitrogen atoms in two different planar configurations, one named FeN₂₊₂/C containing phenanthroline pyridinic N and the other being FeN4/C containing pyrrolic N.^[174] Owing to its nature, the latter is more difficult to incorporate into a graphitic framework, especially in combination with high temperature pyrolysis. Other studies, for instance by Sun et al., also suggested a square-pyramidal coordination of the iron ion with five nitrogen $atoms^{\left[175\right]}$ via DFT calculations. They suggested that a five coordinated Fe centre is more likely to occur due to the high adsorption energy of Fe for a fifth ligand, although it weakens the bonding of O₂. Further, they also found that the Fe centre occurs in the ferrous (Fe²⁺) or ferric state (Fe³⁺) depending on its coordination with four or five ligands, respectively.



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Figure 11. Proposed active sites of metal phthalocyanines catalysts for the oxygen reduction reaction with iron as example. Reproduced with permission from ^[174]. Copyright 2008 Elsevier

Apart from theoretical studies, a number of experimental investigations, mostly employing x-ray absorption fine structure (XANES and EXAFS) and Mössbauer spectroscopy, have shown the involvement of FeN_x/C sites in the oxygen reduction reaction.^[7,87,176–179] Besides FeN_x/C, few research suggests that the active sites are metallic or carbide NPs formed during high temperature pyrolysis surrounded by a protective graphitic layer.^[180,181] More commonly though, findings report a favoured ORR activity for catalysts containing a combination of both, FeN_x/C and Fe NPs.^[56,182] Other research also showed enhanced ORR activity in the presence of iron oxide, often as particles, suggesting the latter could also be a probable active site.^[59,60,183]

Studies using ex and in situ XAFS have given insights into the binding mechanism of O_2 in Fe-containing catalysts, $^{\left[184-187\right]}$ a schematic for the proposed mechanism can be found in Figure 12 both under acidic and alkaline conditions. Here, two different active sites were suggested, one being FeNx/C, active in both electrolytes, and the other being Fe NPs (Fe_{NPs}/C) additionally active at a low pH. Ex situ XAFS found that the Fe-N_x/C sites are present as Fe³⁺N_x/C under aerobic conditions and at high potentials, poisoned with adsorbed oxygen, which switches to the catalytically active Fe²⁺N_x/C at potentials close to the Fe²⁺/Fe³⁺ redox potential, enabling the adsorption of oxygen and initiating the ORR. While the Fe²⁺N_x/C active site enables the first reduction to peroxide intermediates in both electrolytes, they are also responsible for the further reduction of HO2- to OH- under alkaline conditions. Whereas in acidic electrolyte, the second active site Fe_{NPs}/C is needed in close proximity to complete the 4e⁻ reduction pathway. In combination with the powerful X-ray absorption spectroscopy, load-cycling and start-up/shut-down cycling were reported to investigate the degradation mechanisms of structurally and chemically different Fe-NC catalysts.^[188] accelerated stress test identified catalysts based on atomically dispersed metal-N_xC_y (catalysts featuring either only atomically dispersed metal-ion sites) sites are more stable than those with metal@NC sites (catalyst featuring only metal nanoparticles encapsulated in the carbon matrix).



Figure 12. Proposed oxygen reduction reaction pathways determined via in situ XAFS under acidic (blue font) and alkaline (red font) conditions. The schematic includes two types of active sites, FeN_x/C and Fe NPs (Fe_{NPs}/C). Reproduced with permission from ^[166]. Copyright 2018 American Chemical Society

Though most researchers agree that ferrous iron is the active species involved in O_2 binding for ORR, there are contradictory reports relating ferric iron to the adsorption of O_2 . Wang *et al.*^[189] used halogen poisoning with NaF to show that the active sites in their catalyst mainly consist in Fe³⁺ species.

A contentious idea reported in literature is that the metal precursor only helps to create defects in the heteroatom doped carbon framework, promoting "metal-free" C/N active sites, without the metal taking part in the ORR. While few reports present reasonable proof for the actual absence of active metal sites by poisoning experiments or adequate characterisation, [65, 190] most other research studies claim metal-free activity after acid washing/etching via XPS, XRD, TEM or EDX.^[191–193] As discussed earlier, even trace amounts of metal can drastically boost the catalytic activity of a material, thus casting shadow of doubt over the possibility of actual metal-free catalytic activity, particularly when metal precursors were involved in the synthesis. A very recent study carried out by Varnell et al.[194] demonstrated the definitive involvement of Fe in both alkaline and acidic electrolyte in the ORR by selective removal of Fe and remaining content analysis via ICP. They found that a control sample containing 70 % less Fe still exhibited comparable ORR performance in both electrolytes to their standard catalyst, suggesting that only a certain amount (0.2 - 0.5 wt%) of Fe close to the catalyst surface is acting as active sites. Using Fe nitritde, nitric oxide, and hydroxylamine as molecular probes, Malko et al. proved that the active sites for ORR is different under acid and alkaline electrolytes.^[67]

Considering the conflicting claims about the active sites in heteroatom doped carbon catalysts containing Fe, the heterogeneity of such materials still prevents definite assignment.

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Apart from general discussions about active sites, recent findings have indicated the possibility of different active sites depending on the electrolyte due to the common observation that Fe/N@C catalysts show increased activity in alkaline compared to acidic electrolyte, which is often explained by leaching of active sites under acidic conditions, suggesting additional nitrogen functionalities or quinone groups contributing to the catalysts activity.^[195,196] Malko et al. found that poisoning a Fe/N@C catalyst with nitrite or nitric oxide resulted in a drastic activity decrease under acidic conditions, but made little to no difference when tested in alkaline media, which indicated the presence of metal-free active sites under alkaline conditions.^[67] Ramaswamy and Mukerjee^[197] proposed that two distinct ORR mechanisms could take place as a function of electrolyte pH. Specifically, the reaction proceeded via an inner-sphere electron transfer under acidic conditions, while a combination of inner- and outer-sphere electron transfers took place in alkaline media. This was later supported by another research group.^[31] The proposed mechanism can be seen in Figure 13, where the double layer of the inner and outer Helmholtz plane are shown schematically in alkaline media.



Figure 13. Schematic depicting the inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP) in alkaline media showing the inner sphere (a) and outer sphere (b) electron transfer mechanism during the oxygen reduction reaction. Reproduced with permission from ^[197]. Copyright 2019 Hindawi

Under alkaline conditions, hydroxyl, water and chemisorbed oxygen are present at the inner Helmholtz plane.^[197] The inner sphere mechanism (Figure 13a) relies on the chemisorption of oxygen, followed by the complete reduction of adsorbed intermediates until the final product is desorbed, leading to the 4-elecron pathway. The outer sphere mechanism (Figure 13b) involves solvated molecular oxygen, which can interact with

adsorbed surface hydroxyl groups via hydrogen bonds, resulting in the release of peroxide species. Interestingly, the proposed outer sphere mechanism implies a unspecificity towards the nature of the catalyst, e.g. no direct involvement of the metal is assumed. Ramaswamy and Mukerjee further found that for FeN_x catalysts, the inner sphere mechanism was favoured as compared to the outer sphere mechanism, though the formation of stable iron peroxide compounds in alkaline media caused efficient reduction of any intermediate peroxide species, while the reduction of peroxide in acidic media was unlikely due to weak binding between iron and H₂O₂. This explained the improved catalytic activity of FeN_x catalysts in alkaline as compared to acidic media.^[197]

4.3. Atomically dispersed \mbox{FeN}_x for $\mbox{CO}_2\mbox{RR}$ and mechamism study

Regarding the CO₂RR mechanism on Fe-N-C catalysts, many studies proposed that this takes place via a proton-coupled electron transfer process,^[24,89] and the Fe atoms acts as primary centres in stabilizing the reduction intermediates formed, the reaction taking place mostly on M-N sites ^[83,85].

In a recent study Varela and coworkers [24] proposed that the CO2 reduction to CO on Fe-N-C occurs via a decoupled electronproton transfer process (DEPT). The experiments confirming the role of DEPT mechanism were based on the evaluation of CO formation rate as a function of pH, on the reversible hydrogen electrode (RHE) scale (Figure 14Fehler! Verweisquelle konnte nicht gefunden werden.a). Usually, in DEPT reduction an electron transfer is followed by an irreversible protonation step. In this case, they observed an increase in the CO formation rate as the pH shifted towards more basic values, which confirmed the electron-transfer step at higher overpotentials. Considering this outcome, they assumed that CO₂RR towards CO on Fe/N@C type catalysts takes places via a DEPT mechanism, going through an intermediate state (Fe-N-C) - CO2⁻. All the assumptions were corroborated with previous work on CO2RR using Co-N complexes as catalysts^[198,199]. Further, they assumed that the CO2*- intermediates are stabilized by the presence of the K+ ions, facilitating the electrochemical reaction. Finally, the (Fe-N-C) -CO2⁻ intermediate is forming *COOH by protonation, which after reduction give CO (Figure 14Fehler! Verweisquelle konnte nicht gefunden werden.b).

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Figure 14. a) pH dependence of CO formation rate at a constant potential on the NHE scale (black, -0.5 VRHE; red -0.65 VRHE; b) proposed catalytic cycle of the CO2RR on Fe-N-C catalysts. Reproduced with permission from ^[24] Copyright 2018 American Chemical Society

Overall, authors concluded that this mechanism is pH dependent, and by choosing the right pH range, CO₂RR can be directed towards the product of interest, as high selectivities for CO are more common in basic local pH values.^[24] Also, the FeN_x moieties present on the solid-state carbon catalysts are crucial for the stabilization of CO2⁻ intermediates formed during DEPT mechanism. Similar findings were reported by Pan et al. [91] who sought to unveil the nature of the active sites in CO₂RR. Calculating the free-energy evolution of CO₂ reduction to CO, they resumed that the formation of COOH* and CO* intermediates takes place via coupled proton-electron transfer process, in agreement with Varela's results.^[24] In order to evaluate the catalytic activity of Fe-N-C materials, the authors^[91] synthesised M-N-C (M = Fe or Co) and metal free catalysts. By means of EXAFS, XANES, XAS and XPS, they found out that both metals are coordinated with four N atoms in the form of M-N₄ complexes embedded in the carbon structure. By corroborating these findings with previous reports [200,201], they suggested that there are two types of Fe-N₄ formed during the heat treatments synthesis (Figure 15). First, bulk-hosted Fe-N₄ moieties are fully surrounded by C atom. Second, edge-hosted Fe-N₂₊₂ are characterized by two N-doped graphitic layers connected by an Fe atom bonded with two N atoms at the edges of each graphitic layer. The latter structure type causes also a distortion of the carbon plane, leading to an out-of-plane position of Fe.

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Figure 15. Atomic structure of M-N₄-C₁₀ and M-N₂₊₂-C₈ (M=Fe) active sites. Reproduced with permission from ^[91]. Copyright 2018 American Chemical Society

In order to identify the presence of both Fe-N₂₊₂-C₈ and Fe-N₄-C₁₀ in Fe-N-C catalysts, Mössbauer spectroscopy can be used. From XPS came out that the oxidation states of Co and Fe were 2⁺ for Co, and between 2⁺ and 3⁺ for Fe. When tested for CO₂RR, Fe-N-C showed activity at a more positive onset potential (-0.29V) compared to Co-N-C (-0.38V) and N-C (-0.67V). This suggests that Fe-N-C possessed the best intrinsic activity for CO₂RR. The main products identified were CO and H₂ with traces amounts of CH₄. The following FE have been obtained: about 20% for CO on N-C catalysts at -0.79V vs RHE, corresponding to an overpotential of 0.68 V against the standard equilibrium potential of CO₂/CO at -0.11V^[202]: a maximum of 45% towards CO for Co based materials, at 0.48V overpotential, and about 93% at 0.47V overpotential for Fe-N-C. These outcomes indicate that the presence of a metal site helped a lot in suppressing the HER pathway. Also, the large CO current densities on Fe-N-C promotes Fe-N₄ sites as best performing active sites for CO₂RR. Besides their good activity, the stability is also remarkable: a 20h test shows that Fe-N-C is stable for CO FEs of about 93% and a current density of -0.28 mA cm⁻², resulting in about 1.0 mmol cm⁻ ² of CO, at low overpotential (0.47V).

From these conclusions, authors pursued their efforts towards the elucidation of the active sites from F-N-C towards CO_2RR , using DFT calculations. They discovered that the activation energy for COOH dissociation step is way smaller on Fe-N₂₊₂-C₈ sites, compared to Fe-N₄-C₁₀. Also, after calculating the OH adsorption on saturated C atoms of Fe-N₂₊₂-C₈ moieties they suggested that even if the positive heat of reaction is similar to the one obtained for Fe-N₄ sites surrounded by carbon atoms, OH⁻ is more effective for adsorption on the edge sites of carbon is aqueous solution, having strong adsorption affinity for the carbon atoms with dangling bonds next to Fe-N₂₊₂ site, behaviour discussed also by other reports.^[203] Overall, they provided a nice contribution

towards CO₂RR on Fe-N co-doped carbon catalysts, concluding that not only the nature of the metal site is crucial for the evolution of the reduction reaction, but also the type of the metal coordination with the N and C structure is influencing a lot the reduction process.^[91]

The above-mentioned studies are the most representative reports so far to shed to onto the structure of the active sites present in Fe-N-C catalysts for CO₂RR. Other researchers acknowledged that the presence of the metallic centre improves the electrochemical reactivity, either by comparing the catalytic activity with the free-metal catalysts ^[85,86] or by poisoning the active sites^[89]. Huan *et al.*^[85] reported that the content of FeN₄ moieties determines the selectivity for CO over H₂, after testing a series of catalysts containing different amount of Fe in different forms, such as FeN₄ species together with iron carbide, crystalline Fe₂N and Fe_{2+x}N, Fe present as atomically dispersed ions in the N-doped carbon matrix as square-planar Fe^{II}N₄ and Fe^{III}N₄, α -Fe, iron carbide Fe_xC and γ -Fe.

4.4. FeN_x-containing materials for organic reactions

Characterisation of Fe/N@C materials for organic reactions has been comparatively less explored than for electrocatalysis. In the vast majority of the reports in this context, phenantroline-based precursors were used. This resulted in Fe_xO_v NP-containing materials rather than atomically dispersed FeN_x sites, causing a significantly more difficult material characterisation. In the initial report of the Beller group for nitroarene hydrogenation,^[97] the authors had shown by TEM and high-angle annular dark-field imaging microscopy (HAADF) that the material consisted in polydisperse y-Fe₂O₃ NPs surrounded by 3-5 layers of Ncontaining graphene. By XPS, they correlated a high activity with the presence of a nitrogen peak at 399.3eV assigned to a distorted FeN₄ centre.^[204] The presence of FeN₄ centres was maximised at 800°C pyrolysis, with higher temperatures resulting into further decomposition of the active site. Other iron species were detected, including metallic Fe, which stemmed from the reduction of the Fe(OAc)₂ precursor by the carbon support.^[205] Switching to an aminopyr ligand as a precursor, XRD measurements showed the predominance of Fe₃C in the catalyst, along with the iron species previously mentioned.^[99] The Fu group contributed further to the study by performing temperatureprogrammed reduction (TPR) analysis on Fe-phen/C-800. Upon adsorbing H₂ on the material and studying its desorption pattern under a heating ramp, they correlated the presence of FeNx sites with a characteristic peak at 620°C.^[107] However, NH₃ and CO₂ TPR analysis proved inconclusive to detect Lewis acidic and basic sites on the material.[106]

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In the following examples, the authors successfully fabricated and identified atomic FeN_x centres. Deng *et al.* succeeded in making atomically dispersed FeN_x sites over graphene, by embedding iron phthalocyanine (FePc) over graphene nanosheets by ball-milling.^[132] The authors unequivocally confirmed the incorporation of atomic FeN₄ sites into the graphene surface by sub-angstrom resolution high-angle annular dark field – scanning transmission electron microscope (HAADF-STEM, Figure 16A and B) and low-temperature scanning tunneling microscopy (LT-STM, Figure 16C and D) techniques. X-ray absorption fine structure (XAFS) spectroscopy was used to further confirm the similarity of the atomic Fe species to the one of FePc, when XRD and Raman spectroscopy confirmed the absence of FePc, Fe, or FeO_x NP in the material.



Figure 16. Analysis of graphene-embedded FeN4: A) HRTEM of FeN4@C B) Corresponding atomic model C) LT-STL of FeN4@C D) Simulated image. Reproduced from ^[132] Copyright 2018 American Association for the Advancement of Science

Liu *et al.* prepared a mixture of atomic FeN_x centres by depositing Fe(phen)₃ complexes on a nano MgO template, followed by pyrolysis (600-900 °C, 2h) of the material (FeN_x@C). Subsequently, the template and iron oxide NP were removed with HNO₃ (Scheme 6).^[133] By changing the pyrolysis temperature, the authors obtained different mixtures of FeN_x sites, differentiated by their coordination number and their ⁵⁷Fe Mössbauer parameters. Then, they quantified each FeN_x centre amount by KSCN titration.



Scheme 6. FeN_x@C synthesis by templating with MgO NPs.

Under 700°C pyrolysis conditions, the presence of pentacoordinated centres (N-Fe^{III}N₄, D4) was maximised (17.8% of all Fe centres). The presence of this centre is correlated with the highest turnover frequency for benzylic C-H oxidation using *tert*butyl hydrogen peroxide as oxidant (see **Fehler! Verweisquelle konnte nicht gefunden werden.**). Indeed, the authors calculated TOF of D4 to be 6455 h⁻¹, that is 1 order of magnitude higher than the others (2063 h⁻¹ for D1 and 588 h⁻¹ for D2). D3, being fully coordinated, was assumed to be catalytically inactive.

5. Perspective

Fe/N@C nanomaterials constitute a promising class of universal, bio-inspired catalysts. Due to the abundant nature of their three constitutional elements, we are expecting such catalysts to play a major role in the post-fuel chemical industry. Not only Fe, N and C are widely available, they can be found in bio-based precursors that can be treated by HTC or pyrolysis to highly organised materials. They have seen great applications in both electrocatalysis (CO2RR and ORR) as well as diverse organic transformations, putting them in a bright spotlight for renewable feedstock valorisation. With this review, we hope to bridge these two essential fields of catalysis, as well as foster future collaborative investigations. For instance, organic chemists could benefit a lot from the various findings of the electrochemists on material synthesis and single-site identification. In organic catalytic applications, FeNx single site identification has been seldom explored. Future efforts should focus on maximising FeNx site concentration on the carbon support while keeping a high surface area. Indeed, a too high amount of Fe precursor during catalyst synthesis facilitates atomic Fe aggregation, leading to catalytic activity loss. In that regard, switching to self-assembled Fe/N precursors such as MOFs could lead to significant improvements.^[206] The advanced characterisation techniques outlined in section 4 will be invaluable to assert whether FeN_x

single sites are present, in order to maximise turnover numbers. Homogeneous Fe-pincer complexes have been exploited for diverse organic transformations, and may serve as an inspiration for future applications of Fe/N@C. For instance, the hydrogenation scope could be extended to amide, alkene and ester reduction. Since Fe/N@C are active for both oxidations and reductions, they could be applied to complex cascade reactions, such as in the borrowing hydrogen scheme or Guerbet-style condensations. N-coordinated iron complexes have also seen great potential as nitrene insertion and epoxidation catalysts, leaving plenty of room for Fe/N@C-catalysed C-H activation. $^{\ensuremath{\texttt{I207-}}}$ ^{209]} Cross-coupling is the remaining unexplored transformation, and we envision future reports on such reactions using Fe/N@C. An important gap left to address is moving from lab to larger scale. Fe/N@C possesses the intrinsic advantage of being heterogeneous, though flow conditions have to be further explored to establish their scalability. For all the points raised above, discovering new Fe and N precursors will be vital. They will ensure both the economic viability of Fe/N@C and confer control over active site maximisation. Such improvements will facilitate the transition towards commercial systems which can be easily adopted by the chemical industry, to speed up the transition to clean chemicals and fuels.

Keywords: Iron-Nitrogen Complexes • Catalysis • Sustainability • Electrocatalysis • Carbon • Oxygen Reduction •CO₂ Reduction

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Rise of the FeN_x: A new class of heterogeneous catalysts based on abundant elements (Fe,N,C) has been emerging in the past decade. We review here their catalytic applications in both electro- and organic chemistry. Then, we covered various characterisation methods to identify FeN_x active sites.



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Homogenous meets Heterogenous and Electro-Catalysis: Iron-nitrogen molecular complexes within carbon materials for catalytic applications

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