The evolution pathway from iron compounds to Fe₁(II)-N₄ sites through gas-phase iron during pyrolysis

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ABSTRACT: Pyrolysis is indispensable for synthesizing highly active Fe-N-C catalysts for the oxygen reduction reaction (ORR) in acid, but how Fe, N, and C precursors transform to ORR-active sites during pyrolysis remains unclear. This knowledge gap obscures the connections between the input precursors and output products, clouding the pathway toward Fe-N-C catalyst improvement. Herein, we unravel the evolution pathway of precursors to ORR-active catalyst comprised exclusively of single atom Fe₁(II)-N₄ sites via in-temperature X-ray absorption spectroscopy. The Fe precursor transforms to Fe oxides below 300 °C, and then to tetrahedral Fe₁(II)-O₄ via a crystal-to-melt-like transformation below 600 °C. The Fe₁(II)-O₄ releases a single Fe atom that flows into the N-doped carbon defect forming Fe₁(II)-N₄ above 600 °C. This vapor phase single Fe atom transport mechanism is verified by synthesizing Fe₁(II)-N₄ sites via “non-contact pyrolysis” wherein the Fe precursor is not in physical contact with the N and C precursors during pyrolysis.

INTRODUCTION

Hydrogen fuel cell vehicles (FCVs), based on proton exchange membrane fuel cells (PEMFCs), were first sold commercially in Japan in 2014 with the launch of the Toyota Mirai,¹ followed by limited commercialization in Europe, Korea, Canada, and the United States in 2015 by both Toyota and Hyundai. The catalysts used for the oxygen reduction reaction (ORR) in PEMFCs are Pt-alloys.¹ While advances have been made in reducing platinum usage in PEMFCs, the cost of automotive fuel cell systems is still prohibitively high, due primarily to the high loading of Pt on the PEMFC cathode.^{1,2} The key to widespread and sustainable commercialization of FCVs from a cost perspective is the significant reduction of Pt loading,² or replacing Pt-alloys with earth-abundant, inexpensive materials (i.e., platinum group metal (PGM)-free). The leading PGM-free catalysts for the ORR in PEMFCs are single transition metal atoms (M=Mn, Fe or Co) embedded in a nitrogen-doped carbon matrix (M-N-C).³⁻⁹ Recently, Ye *et al.*⁹ reported a Fe-N-C catalyst that delivers 570 mW·cm⁻² in H₂/air PEMFCs. Nevertheless, this state-of-the-art performance is insufficient for automotive PEMFCs.² Further progress in performance necessitates improvements in the turnover frequency and/or in the density of active sites in M-N-C materials, both of which are impeded by the lack of rational synthesis of M-

N-C catalysts. The current synthesis strategies for M-N-C catalysts consist of combining sources of M, N, and C either in a single compound or in separate compounds and pyrolyzing the compound(s) typically in the 900 to 1100 °C temperature range.^{6-8, 10, 11} These synthesis strategies primarily rely on an empirical approach of precursor identity, M content, and pyrolysis settings to increase catalytic activity. The underlying mechanism governing the competitive formation of metal-based active sites and byproducts during pyrolysis has remained elusive. Rational synthesis of improved M-N-C catalysts requires unraveling the current “black box” synthesis approach of input precursors and output products.

The complexity of M-N-C catalyst structures arises largely from the pyrolysis process, which was demonstrated in the 1980s to be essential to producing highly active M-N-C catalysts for the ORR in acidic media.¹¹ The material resulting from the high temperature pyrolysis, however, is often a mixture of species including N-doped carbon defects or edges, M-N_x moieties, and inorganic particles of metal, metal oxides, carbides, nitrides, *etc.*¹²⁻¹⁷ All these species have been proposed to be ORR active in alkaline and even in acidic electrolyte.^{3, 10, 12-19} It thus remains inconclusive which site(s) are responsible for the superior ORR activity of M-N-C catalysts. This issue has been addressed by efforts to gain some control

over the final products. By lowering the Fe content in the precursors (<1 wt%), some research groups managed to produce Fe-N-C catalysts with predominately Fe₁(II)-N₄ (Fe₁ denotes the single atom configuration without direct Fe-Fe bonds) moieties, as evidenced by ⁵⁷Fe Mössbauer and X-ray absorption spectroscopy (XAS).^{6, 10, 19, 20} These catalysts exhibit high ORR performance despite their low gravimetric and volumetric density of Fe₁(II)-N₄ sites. Lately, Fe₁(II)-N₄ moieties were visualized in the Fe-N-C catalyst by scanning transmission electron microscopy coupled with electron energy loss spectroscopy.³ These studies indicate that the Fe₁(II)-N₄ moiety has a high turnover frequency towards the ORR and likely is the major contributor to the ORR activity of pyrolyzed Fe-N-C catalysts. This finding identifies an obvious pathway towards Fe-N-C catalyst advancement via increasing the Fe₁(II)-N₄ site density. However, the electrochemically active Fe₁(II)-N₄ site density saturates at a very low Fe content (< 3 wt%),^{6, 20} despite substantial efforts to optimize the type and composition of precursors and pyrolysis conditions. The marginal improvement in Fe-N-C catalysts reported in the last years with trial-and-error synthesis approach calls for a return to the original question: how is the Fe₁(II)-N₄ site formed during pyrolysis? Herein, we directly monitor the stepwise transformation from Fe precursors to Fe₁(II)-N₄ sites during pyrolysis and validate our site formation mechanistic model via “non-contact pyrolysis” where the Fe and C-N precursors are not in physical contact during pyrolysis.

RESULTS AND DISCUSSION

In-temperature XAS was conducted on the mixture of Fe, N, and C precursors at the Fe K-edge throughout the pyrolysis and cooling processes. We gradually increased the temperature of the samples to 1000 °C and then decreased the temperature to room temperature in a flowing Helium atmosphere, holding at targeted temperatures during XAS measurements. Two different routes were chosen for *in-temperature* XAS measurements. The first route used a mixture of iron(II) acetate (FeAc₂), 1,10-phenanthroline monohydrate, and a Zn-based metal organic framework (MOF), zeolitic imidazolate framework eight (ZIF-8), mixed *via* ball milling (see Supplementary). These precursors are typical for synthesis of MOF-derived Fe-N-C catalysts^{6, 8, 10, 15, 20} and have been shown to generate active Fe-N-C catalysts with predominantly Fe₁(II)-N₄ sites.^{6, 10, 20} However, with this route, the thermal evolution of the Fe compound is convoluted with the thermal evolution of the N and C precursors. To deconvolute the effect of pyrolysis on the Fe and C-N constituents, the second route used a mixture of FeCl₂·4H₂O, as the iron precursor not containing N and C, and a heat-treated N-doped carbon matrix (N-C) as the N and C precursor. Following the procedure developed for pyrolysis of MOF-derived Fe-N-C catalysts,^{10, 20} the N-C was synthesized by homogenizing ZIF-8 and 1,10-phenanthroline dry powders *via* low-energy planetary ball-milling, followed by heat treatment in Ar at 1050 °C for one hour and a second heat treatment in NH₃ at 900 °C for 15 minutes. Multiple characterizations (Figure S1) showed that the N-C has a porous structure with a Brunauer-Emmett-Teller (BET) surface area of 950 m²·g⁻¹, of which 770 m²·g⁻¹ is contributed from micropores according to the t-plot analysis (Figure S1E). X-ray photoelectron spectroscopy (XPS) indicated 0.46 at% of residual Zn, 2.86 at% of O, 6.51 at% of N, and in particular an ultra-high content of pyridinic N as manifested by the prominent peak at 398.3 eV (Figure S1D).²¹ The simultaneous presence of abundant micropores and pyridinic N preferentially located at the defects and edges of the carbon

matrix²² signifies the presence of abundant nitrogen-doped microporous defects.²¹

XAS of the FeCl₂·4H₂O and N-C mixture. As compared to the as-received FeCl₂·4H₂O, the FeCl₂·4H₂O mixed with N-C *via* ball milling exhibits a much lower peak intensity of the X-ray absorption near edge structure (XANES) spectrum at room temperature (Figure 1A). Meanwhile, the intensity of the Fe-O (O from H₂O) scattering, with a peak at approximately 1.5 Å in the Fourier transform of the extended X-ray absorption fine structure (FT-EXAFS, note that the distances in the FT-EXAFS are not corrected for phase shift), drops dramatically; whereas the Fe-Cl scattering peak around 2.1 Å largely remains unchanged (Figure 1B). These results indicate the partial detachment of the ligating water molecules upon ball milling. As the temperature increases to 300 °C (denoted as FeCl₂-NC-300), the Fe-Cl scattering peak disappears, and new peaks emerge. The Fe-O peak at 1.4 Å and the newly emerging Fe-Fe peaks at 2.7 Å and 4.6 Å overlap those of the α-Fe₂O₃ standard (Figure 1B). Meanwhile, the edge energy increases and the XANES spectrum approaches that of α-Fe₂O₃ (Figure 1A). These results verify the formation of ferric oxides at 300 °C. As the temperature gradually increases to 600 °C, the XANES shifts to lower energy approaching that of the Fe(II)O standard (Figure 1A), indicating the reduction of ferric oxides to ferrous oxides. The intensities of both the Fe-O and Fe-Fe peaks drop, with the Fe-Fe peaks eventually disappearing at 600 °C, leaving behind one prominent peak at 1.5 Å (Figure 1B). The peak can be well fit with an Fe-O path with a bond distance of 1.99 ± 0.01 Å and a coordination number of 3.6±0.4 (Table S2 and Figure S2). This Fe-O configuration was previously reported, in molten Fe salts, to be a tetrahedral Fe(II)-O₄ moiety with an Fe-O bond distance of 1.98±0.02 Å.²³ The tetrahedral structure of the Fe₁(II)-O₄ species observed at 600 °C is supported by the high intensity of the 1s → 3d transition feature of XANES at 7112 eV, as this feature is minimal for centrosymmetric Fe species, such as in-plane Fe₁(II)-N₄ in iron phthalocyanine (FePc), and is intense in non-centrosymmetric Fe species, especially for the tetrahedral geometry (Figure S3).^{13, 23} The observed transition from ferric oxides with a local structure of octahedral Fe-O₆, with Fe-Fe bonds, to tetrahedral Fe₁(II)-O₄ without Fe-Fe bonds, is akin to the crystal-to-melt transition of Fe salts to Fe(II)-O₄ upon melting above 1300 °C.²³ Here the Fe₁(II)-O₄ is not in a molten state since it is observed at much lower temperature. Moreover, Fe₁(II)-O₄ is unstable by itself owing to the unbalanced cationic and anionic charge. It is rather stabilized by N-C in a solid state *via* electron delocalization that restores the charge balance such as is observed for Fe₁(II)-N₄ sites imbedded in a graphene plane.¹⁶

The in-plane Fe₁(II)-N₄ moieties emerge at approximately 600 °C. This is signified by the appearance of a peak at 7117 eV in the first derivative of the XANES spectra, overlapping that of the FePc standard (Figure 1C). This signal arises from the 1s → 4p_z transition with simultaneous ligand to metal charge transfer, and is the fingerprint of the in-plane Fe₁(II)-N₄ structure.^{12, 13} As the temperature increases to 1000 °C, the XANES spectrum at energies just above 7117 eV transition gradually shifts to higher energies approaching that of FePc (Figure 1A), indicating the transformation from the tetrahedral Fe₁(II)-O₄ to in-plane Fe₁(II)-N₄. This shift continues rather than reverses during cooling to room temperature, which indicates that the Fe₁(II)-O₄ → Fe₁(II)-N₄ transformation is an irreversible thermal process. After cooling to room temperature, but before exposure to air, the Fe speciation (FeCl₂-NC-End) is dominated in-plane Fe₁(II)-N₄ moieties, as verified by

both the XANES and EXAFS spectra. The in-plane $\text{Fe}_1(\text{II})\text{-N}_4$ fingerprint shoulder of $\text{FeCl}_2\text{-NC-End}$ at 7117 eV becomes prominent in the first derivative of the XANES (Figure 1C) and even discernible in the XANES spectrum (Figure 1A). The EXAFS fitting (Figure S6) gives a first shell Fe-N coordination number of 4.3 ± 0.4 and bond length of 1.91 ± 0.01 Å, close to that of FePc (1.93 ± 0.01 Å).²⁰ This Fe-N bond distance is much shorter than that of Fe-O (1.99 ± 0.01 Å) as expected from the in-plane structure versus the tetrahedral structure.

Figure 1. (A) XANES, (B) Fourier Transform (FT)-EXAFS and (C) the first derivative of the XANES spectra of $\text{FeCl}_2\text{-NC-T}$ collected with temperature increasing from room temperature to 1000 °C and cooling down to room temperature. (D) ^{57}Fe Mössbauer spectrum (5 K) and fitting of $\text{FeCl}_2\text{-NC-Air}$. (E) ORR performance of $\text{FeCl}_2\text{-NC-T}$ catalysts. RDE polarization plots were obtained in room temperature O_2 -saturated 0.1 M HClO_4 from 0.05 to 1.05 V with a scan rate of $1 \text{ mV} \cdot \text{s}^{-1}$ at a rotation rate of 1,600 rpm. The corresponding cyclic voltammograms are displayed in Figure S4.

Upon exposure to air ($\text{FeCl}_2\text{-NC-Air}$), the XANES spectrum shifts positively and the fingerprint shoulder at 7117 eV becomes barely discernible (Figure 1A), indicating the oxidation of the majority of the $\text{Fe}_1(\text{II})\text{-N}_4$ via adsorption of an O_2 ligand, forming $\text{Fe}_1(\text{III})\text{-N}_4\text{-O}_2$ sites. Low temperature (5 K) *ex situ* Mössbauer identifies two doublets D1 and D2 in $\text{FeCl}_2\text{-NC-Air}$ (Figure 1D and Table S3). The D1 and D2 are the most common doublets identified in Fe-N-C materials, and have been recently assigned to $\text{Fe}_1(\text{III})\text{-N}_4\text{-O}_2$ and $\text{Fe}_1(\text{II})\text{-N}_4$, respectively.^{10,24} These combined results conclusively confirm the formation of gas-phase accessible in-plane $\text{Fe}_1(\text{II})\text{-N}_4$ upon pyrolysis at temperatures $>600^\circ\text{C}$.

In parallel, X-ray diffraction (XRD) measurements were conducted on the same mixture after being subjected to pyrolysis at various maximum temperatures. No Fe-related signals are observed throughout the temperature range up to 1000 °C

(Figure S7). This result indicates the lack of long-range order structures of all the Fe species including the oxides observed by XAS, which is consistent with the lack of prominent FT-EXAFS peaks at high R values (Figure 1B). The ORR activities of these mixtures were assessed in a rotating disk electrode (RDE) in an O_2 -saturated 0.1 M HClO_4 electrolyte. The ORR activities of the catalysts pyrolyzed at 200 °C and 400 °C are no better than that of N-C (Figure 1E). The ORR activity improves dramatically as the pyrolysis temperature increases to 600 °C, coinciding with the emergence of $\text{Fe}_1(\text{II})\text{-N}_4$ sites. The activity continues to improve with increasing temperature up to 1000 °C, reaching a half-wave potential of 0.8 V (all the potentials reported here are versus the reversible hydrogen electrode and are not IR-corrected) (Figure 1E), which coincides with the increasing transformation from $\text{Fe}_1(\text{II})\text{-O}_4$ to $\text{Fe}_1(\text{II})\text{-N}_4$. Not only is the activity comparable to those of state-of-the-art Fe-N-C catalysts in RDE measurements,^{3, 6, 25} but the intimate correlation between the increasing ORR activity and the increasing relative content of $\text{Fe}_1(\text{II})\text{-N}_4$ in the sample provides startling evidence that the $\text{Fe}_1(\text{II})\text{-N}_4$ moiety is responsible for the high ORR activity of Fe-N-C in acidic electrolyte.

Nearly the same thermal evolution process was observed in the *in-temperature* XAS experiment on the MOF-based mixture: $\text{FeAc}_2 \rightarrow$ ferric oxides with a local octahedral Fe-O_6 structure $\rightarrow$ ferrous oxides $\rightarrow$ tetrahedral $\text{Fe}_1(\text{II})\text{-O}_4 \rightarrow$ in-plane $\text{Fe}_1(\text{II})\text{-N}_4$ (Supplementary Section 3). The two different but representative groups of Fe, N, and C precursors undergoing the same thermal evolution pathway suggests that this is likely a common pathway towards the formation of $\text{Fe}_1(\text{II})\text{-N}_4$ upon the pyrolysis of the mixture of Fe, N, and C precursors. This pathway is however obscured by the missing link between the tetrahedral $\text{Fe}_1(\text{II})\text{-O}_4$ and in-plane $\text{Fe}_1(\text{II})\text{-N}_4$. The question remains as to how the $\text{Fe}_1(\text{II})\text{-O}_4$ transforms to a moiety with a very different local geometry and ligand environment. An alternative transformation from tetrahedral Fe-N_4 to active FeN_4 was recently proposed to occur at temperatures ≥ 800 °C during the pyrolysis of Fe-doped ZIFs to form Fe-N-C catalysts.⁶ EXAFS cannot distinguish the Fe-O_4 structure from Fe-N_4 since it cannot distinguish O from N as scattering neighbors.

To address this uncertainty, we conducted the *in-temperature* XAS on the mixture of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and nanoscale SiO_2 powders in an environment free of N and C. The SiO_2 was deliberately chosen to dilute $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ for XAS measurements in the transmission mode, as it can also serve as a support with high thermal stability as an alternative to N-C.^{13,23} The thermal evolution involving the decomposition of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ towards the formation of one prominent peak around 1.4 Å at 600 °C was again observed (Figure 2A). The fitting of the EXAFS spectrum at 600 °C gives an Fe-O coordination number of 3.9 ± 0.6 and bond length of 2.00 ± 0.02 Å (Table S5), thus conclusively confirming the formation of tetrahedral $\text{Fe}_1(\text{II})\text{-O}_4$ rather than $\text{Fe}_1(\text{II})\text{-N}_4$ or $\text{Fe}_1(\text{II})\text{-C}_4$. More importantly, this XAS spectrum at 600 °C ($\text{FeCl}_2\text{-SiO}_2\text{-600}$) nearly overlaps that of the $\text{FeCl}_2\text{-NC-600}$, with trivial differences arising from a small fraction of $\text{Fe}_1(\text{II})\text{-O}_4$ having already converted to $\text{Fe}_1(\text{II})\text{-N}_4$ in $\text{FeCl}_2\text{-NC-600}$ (Figure 2A and Figure S12). This result thus verifies the formation of $\text{Fe}_1(\text{II})\text{-O}_4$ upon the pyrolysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ mixed with either N-C or SiO_2 and, by inference, pyrolysis of the $\text{FeAc}_2\text{-ZIF-8}$ mixture.

As the temperature of the $\text{FeCl}_2\text{-SiO}_2$ mixture increases from 600 °C to 1000 °C, in the absence of N-C the $\text{Fe}_1(\text{II})\text{-O}_4$ partly transforms to ferrous oxides and then Fe nanoparticles, rather than $\text{Fe}_1(\text{II})\text{-N}_4$ (Figure 2A) (Supplementary Section 4). The

$\text{Fe}_1(\text{II})\text{-O}_4$ and Fe nanoparticles are present throughout the cooling to room temperature, as seen in Figure 2B, wherein the growth of the FT-EXAFS peaks is mainly caused by the decreasing Debye-Waller factor with decreasing temperature. The XANES spectra remain largely unchanged during cooling (Figure S11B). The presence of $\text{Fe}_1(\text{II})\text{-O}_4$ at room temperature verifies that it is a stable species when anchored onto a substrate. The thermal evolution pathway of the FeCl_2 mixed with SiO_2 mixture may represent a typical synthesis process of single atom catalysts supported on oxides.

Figure 2. FT-EXAFS spectra of $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ mixed with SiO_2 collected with (A) temperature increasing from room temperature to 1000 °C together with and (B) cooling down to room temperature. (C) Schematic illustration of the common pathways up to 600 °C of the thermal evolution of iron compounds during pyrolysis, and then diverging pathways at $T \geq 600^\circ\text{C}$ depending on the absence or presence of N-C defects.

Collectively, the thermal evolution of the Fe precursors in the three mixtures converges to the formation of tetrahedral $\text{Fe}_1(\text{II})\text{-O}_4$ at 600 °C, and then diverges at higher temperatures with/without N-C (Figure 2C). This thermal decomposition generally follows the Fe-O phase diagram that depicts the transformation of ferric oxides to ferrous oxides around 300 °C in an oxygen-deficient gaseous environment and then to Fe nanoparticles around 600 °C with all the oxygen neighbors removed.^{26, 27} A natural hypothesis deduced from the Fe-O phase diagram is that the complete removal of the oxygen neighbors from $\text{Fe}_1(\text{II})\text{-O}_4$ leaves behind a single free Fe atom (Fe_1), which may form $\text{Fe}_1(\text{II})\text{-N}_4$ if captured by the N-C defect nearby: $\text{Fe}_1(\text{II})\text{-O}_4 \rightarrow \text{Fe}_1 \rightarrow \text{Fe}_1(\text{II})\text{-N}_4$, or sinter into aggregated Fe clusters in the absence of N-C defects (Figure 2C).

A unique aspect of this so-called impregnation mechanism lies in the formation of Fe_1 . The Fe_1 is essentially a gas phase iron that expands to fill the volume available, from which we deduce that it is not necessary to mix the Fe precursors with N

and C during pyrolysis to produce active Fe-N-C catalysts, as previously asserted, since the Fe_1 released from the Fe precursor can flow into the N-C defects forming $\text{Fe}_1(\text{II})\text{-N}_4$. To test this hypothesis, we developed non-contact pyrolysis wherein the Fe precursor and N-C are separately placed in two boats in the furnace without direct physical contact during pyrolysis (Figure 3A). In addition to FeAc_2 and $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$, that were shown above to transform to $\text{Fe}_1(\text{II})\text{-N}_4$ sites when mixed with N and C precursors, $\alpha\text{-Fe}_2\text{O}_3$ was also investigated as the Fe precursor since ferric oxides were observed at intermediate temperature on both synthesis routes during *in-temperature* XAS.

Figure 3. (A) Schematic illustration of the non-contact pyrolysis wherein the Fe precursor and N-C were separately placed in two boats in the furnace during pyrolysis with Fe placed upstream of the gas flow. (B) ORR performance of indicated catalysts. RDE polarization plots were obtained in room-temperature O_2 -saturated 0.1 M HClO_4 from 0.05 to 1.05 V with a scan rate of $1 \text{ mV}\cdot\text{s}^{-1}$ at a rotation rate of 1600 rpm. Solid lines represent catalysts obtained by non-contact pyrolysis; dashed line catalysts obtained by regular pyrolysis for comparison. (C) $\text{H}_2\text{-O}_2$ and (D) $\text{H}_2\text{-air}$ fuel cell polarization curves. Cathode: $\sim 4.0 \text{ mg}\cdot\text{cm}^{-2}$ of $\text{FeCl}_2/\text{NC-1000}$; Anode: $0.3 \text{ mg}_{\text{Pt}}\cdot\text{cm}^{-2}$ Pt/C; Membrane: NR212 membrane (Ion Power); 200 and $1000 \text{ mL}\cdot\text{min}^{-1}$ gas fed with 100% RH at anode (H_2) and cathode (O_2/air), respectively; electrode area 5 cm^2 . The back pressures during the fuel cell tests are 1.0 bar reactant gas. (E) XANES and (F) FT-EXAFS spectra of the three catalysts obtained by non-contact pyrolysis, and of the Fe foil and FePc-O_2 . (G) TGA of the three Fe precursors including $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$, FeAc_2 , and $\alpha\text{-Fe}_2\text{O}_3$.

The ORR performance of the N-C subjected to the non-contact pyrolysis with $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ at 1000 °C (denoted as $\text{FeCl}_2/\text{NC-1000}$) is essentially the same as that of the mixture of $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ and N-C pyrolyzed at 1000 °C ($\text{FeCl}_2\text{-NC-}$

1000) (Figure 3B). This catalyst also exhibits decent performance in PEMFCs. It delivers an IR-corrected current density of $105 \text{ mA} \cdot \text{cm}^{-2}$ and $400 \text{ mA} \cdot \text{cm}^{-2}$ at 0.8 V and 0.7 V, respectively, in a H_2 - O_2 PEMFC (Figure 3C), and a maximum power density of $0.28 \text{ W} \cdot \text{cm}^{-2}$ in a H_2 -air PEMFC (Figure 3D). This relatively high performance achieved right away is likely related to the enriched surface active sites as expected from the surface vapor deposition feature of the non-contact pyrolysis. This is the first demonstration of a highly active Fe-N-C PEMFC cathode catalyst that is synthesized without mixing the Fe precursor with N and C precursors. Driven by the proof-of-concept, optimizations of the precursors, non-contact pyrolysis, and the corresponding PEMFC testing are undergoing in our groups.

The formation of $\text{Fe}_1(\text{II})\text{-N}_4$ in the non-contact pyrolysis material, as reflected by the RDE and PEMFC results, is confirmed by the post-pyrolysis XAS measurements. The amount of Fe deposited onto N-C is $\sim 1.5 \text{ wt}\%$ as estimated from the edge step of the XANES, and $\sim 1.8 \text{ wt}\%$ by the X-ray fluorescence (XRF). The XANES aligns well with that of Iron(III) phthalocyanine-tetrasulfonic acid (FePc-O_2) (Figure 3E). Correspondingly, the EXAFS shows a prominent Fe-N/O peak around $1.5 \text{ \AA}$ that nearly overlaps the Fe-N/O scattering peak of FePc-O_2 (Figure 3F). The small Fe-Fe peaks indicate the co-presence of Fe nanoparticles and oxides, which are evident in the XRD pattern (Figure S14). These results demonstrate that the non-contact pyrolysis produces highly active Fe-N-C catalysts with predominantly $\text{Fe}_1(\text{II})\text{-N}_4$ sites, thereby supporting the proposed gas phase transport-impregnation mechanism.

The ORR activity of the N-C subjected to the non-contact pyrolysis with $\alpha\text{-Fe}_2\text{O}_3$ at 1000°C ($\text{Fe}_2\text{O}_3\backslash\text{NC-1000}$) is much higher than that of N-C; it is worse than that of $\text{FeCl}_2\text{-NC-600}$, but with the same onset potential (Figure 3B). This suggests the presence of $\text{Fe}_1(\text{II})\text{-N}_4$ sites as in $\text{FeCl}_2\text{-NC-600}$, but with lower site density. Indeed, the XANES and EXAFS of $\text{Fe}_2\text{O}_3\backslash\text{NC-1000}$ nicely overlap with those of the $\text{FeCl}_2\backslash\text{NC-1000}$ and FePc-O_2 (Figure 3E and 3F), confirming the formation of $\text{Fe}_1(\text{II})\text{-N}_4$. The trivial edge step of the XANES indicates small amounts of Fe deposited on N-C, which is estimated at approximately $0.03 \text{ wt}\%$ by XRF. This is expected from the high thermal stability of $\alpha\text{-Fe}_2\text{O}_3$ with a decomposition temperature higher than 1000°C , as seen by the thermogravimetric analysis (TGA) results (Figure 3G). These results further support the gas phase transport-impregnation mechanism by validating the non-contact pyrolysis using $\alpha\text{-Fe}_2\text{O}_3$. They also indicate that ionic compounds with stable crystalline structures are not ideal Fe precursors for Fe-N-C synthesis due to the high energies needed to break the stable Fe-Fe bonds to release Fe_1 . It was recently shown that metal (Pd or Ni) nanoparticles can release single free metal atoms that form metal- N_4 sites upon impregnation into N-C defects, but this only occurs at $>1000^\circ\text{C}$ as the competitive sintering process dominates at lower temperatures.^{28, 29}

However, the thermal stability of the ferric oxides generated *in situ* from the two routes is much lower than that of $\alpha\text{-Fe}_2\text{O}_3$ as it is readily reduced to $\text{Fe}_1(\text{II})\text{-O}_4$ with the Fe-Fe bonds cleaved as the temperature increases from 300°C to 700°C (Figure 1B and Figure S8B). Note that the ferric oxides generated *in situ* are invisible to XRD (Figure S7), which indicates the clusters are ultra-small and/or amorphous. We thus deduce that the N-C disturbs the long-range crystalline structure of Fe oxides thereby weakening the Fe-Fe bonds, and/or trap small Fe oxides with reduced number of Fe-Fe bonds, promoting the transformation from Fe-O_6 with less and weakened Fe-Fe

bonds to $\text{Fe}_1(\text{II})\text{-O}_4$. In addition, the stabilization of $\text{Fe}_1(\text{II})\text{-O}_4$ in a solid state by the N-C or SiO_2 substrate further promotes the crystal-to-melt-like transformation of $\text{Fe-O}_6 \rightarrow \text{Fe}_1(\text{II})\text{-O}_4$ at much lower temperatures. Without N-C, the $\alpha\text{-Fe}_2\text{O}_3$ with stable crystalline structures releases few Fe_1 atoms and thus forms few $\text{Fe}_1(\text{II})\text{-N}_4$ sites at 1000°C .

The ORR performance of the N-C subjected to the non-contact pyrolysis with FeAc_2 at 1000°C is slightly better than that of N-C but much worse than that of $\text{Fe}_2\text{O}_3\backslash\text{NC-1000}$ (Figure 3B), indicating the absence of $\text{Fe}_1(\text{II})\text{-N}_4$. Both XAS (Figure 3E and 3F) and XRD (Figure S14) measurements on the N-C after the non-contact pyrolysis show the presence of a mixture of Fe nanoparticles and oxides as the predominant Fe species. The Fe content is around $0.5 \text{ wt}\%$ as estimated from the edge step of the XANES and the XRF. These results indicate that Fe_1 atoms were also released from FeAc_2 , and flow onto the N-C forming Fe clusters rather than $\text{Fe}_1(\text{II})\text{-N}_4$. One key difference between FeAc_2 and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ or $\alpha\text{-Fe}_2\text{O}_3$ is that the former decomposes at $\sim 300^\circ\text{C}$, whereas the latter ones decompose above 600°C (Figure 3G). Consequently, the Fe_1 released from $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ or $\alpha\text{-Fe}_2\text{O}_3$ upon the decomposition meets the N-C at temperatures higher than the threshold temperature of the formation of $\text{Fe}_1(\text{II})\text{-O}_4$ ($>400^\circ\text{C}$) and $\text{Fe}_1(\text{II})\text{-N}_4$ ($\sim 600^\circ\text{C}$), eventually forming $\text{Fe}_1(\text{II})\text{-N}_4$ at 1000°C . On the other hand, the Fe_1 was released from FeAc_2 at $\sim 300^\circ\text{C}$. At such low temperature sintering of Fe_1 into aggregated clusters dominates,²⁸ leading to the formation of Fe nanoparticles. This side-effect is however overcome by mixing FeAc_2 with N and C precursors during pyrolysis, wherein the N-C stabilizes the $\text{Fe}_1(\text{II})\text{-O}_4$ as the reservoir of Fe_1 throughout a wide temperature range of $400\text{--}1000^\circ\text{C}$ (Figure S8), promoting the formation of $\text{Fe}_1(\text{II})\text{-N}_4$. An important implication from these results is that the threshold temperature of the formation of $\text{Fe}_1(\text{II})\text{-N}_4$ around 600°C is determined by the threshold temperature of the impregnation of Fe_1 into the N-C defect ($\text{Fe}_1 \rightarrow \text{Fe}_1(\text{II})\text{-N}_4$), rather than the release temperature of Fe_1 . That is, it is determined by the inherent thermal stability of $\text{Fe}_1(\text{II})\text{-N}_4$. The $\text{Fe}_1(\text{II})\text{-O}_4$ has a lower thermal stability as it forms and decomposes at lower temperatures. The different thermal stability between $\text{Fe}_1(\text{II})\text{-N}_4$ and $\text{Fe}_1(\text{II})\text{-O}_4$ accounts for the competition between them during the pyrolysis above 600°C , and the $\text{Fe}_1(\text{II})\text{-N}_4$ gradually wins the competition as the temperature increases to 1000°C . This fundamental limitation determines the necessity of multiple pyrolysis with optimized temperature around 1000°C to drive the $\text{Fe}_1(\text{II})\text{-O}_4 \rightarrow \text{Fe}_1(\text{II})\text{-N}_4$ transformation.

CONCLUSION

We unraveled the thermal evolution pathway during the pyrolysis of Fe-N-C catalysts: Fe precursor $\rightarrow$ Fe oxides (octahedral Fe-O_6) $\rightarrow$ tetrahedral $\text{Fe}_1(\text{II})\text{-O}_4$ $\rightarrow$ Fe_1 $\rightarrow$ $\text{Fe}_1(\text{II})\text{-N}_4$. The demonstration of the non-contact pyrolysis reveals the presence of gas phase iron at mild temperatures; and opens up an avenue for the synthesis of single-atom catalysts *via* vapor deposition approaches.

ASSOCIATED CONTENT

Supporting Information

Supporting information (PDF) includes: Experimental Section; Results and Discussion: Section 1. N-C Characterizations (Figure S1); Section 2. In-temperature XAS on the mixture of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and N-C (Figure S2-S7 and Table S2-S3); Section 3. In-temperature XAS on the mixture of MOF-based mixture (Figure S8-S10 and Table S4); Section 4. In-temperature XAS on the mixture of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and SiO_2 (Figure S11-S13 and Table S5);

Section 5. Non-contact pyrolysis of three different Fe precursors (Figure S14). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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Supporting Information

Experimental Section

Synthesis.

Chemicals: Fe(II) acetate ($\text{Fe}(\text{CO}_2\text{CH}_3)_2$, $\geq 99.99\%$) (denoted as FeAc_2), 1,10-phenanthroline monohydrate, Zn-based zeolitic imidazolate framework (ZIF-8), Iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 99.99%), iron(III) oxide ($\alpha\text{-Fe}_2\text{O}_3$), iron(II) phthalocyanine (FePc), Iron(III) phthalocyanine-tetrasulfonic acid (FePc-O_2), silicon dioxide (SiO_2 , 4 mm, 99.99%), zinc oxide (ZnO), 2-methylimidazole, and perchloric acid (HClO_4 , 70%, PPT Grade) were all purchased from Sigma-Aldrich. All aqueous solutions were prepared using deionized (DI) water ($18.2 \text{ M}\Omega \cdot \text{cm}$) obtained from an ultra-pure purification system (Aqua Solutions).

Synthesis of the Fe-MOF precursor: The detailed synthesis of the Fe-MOF precursor was reported by us previously.¹⁰ Summaries of the amounts of reactants for Fe-MOF precursor is given in Table S1. Briefly, 0.81 g zinc oxide (pre-treated at 400°C in air before use), 1.64 g 2-methylimidazole, and 0.053 g ammonia sulfate were ball milled for one hour in the presence of 100 μL methanol. A 75 mL polypropylene grinding vial and two 3/8-inch methacrylate balls were used as the container and the grinding media, respectively. Subsequently, 0.0435 g FeAc_2 and 3.60 g 1,10-phenanthroline monohydrate were added and ball milled for two hours. The resulting precursor was subjected to the *in-temperature* XAS measurements.

Table S1. Summaries of the amounts of reactants for Fe-MOF precursor.

	ZnO	2-methyl- imidazole	1,10- phenanthroline	FeAc_2	$(\text{NH}_4)_2\text{SO}_4$
MW (g/mol)	81.408	82.080	180.07	173.930	132.14
Eq.	1	2	2	0.025	0.04
n (mmol)	10	20	20	0.25	0.4
m (g)	0.8141	1.6416	3.6014	0.0435	0.0529

Synthesis of N-C: 200 mg of 1,10-phenanthroline and 800 mg of ZIF-8 were weighed and poured into a ZrO₂ crucible with one hundred zirconium-oxide balls of 5 mm diameter. The ZrO₂ crucible was then sealed under air and placed in a planetary ball-miller (Fritsch Pulverisette 7 Premium, Fritsch, Idar-Oberstein, Germany). The powders were milled for 4 cycles of 30 min at 400 rpm milling speed. The precursor resulting from the milling was first pyrolyzed at 1050 °C in Ar for 1 hour with a ramp rate of 5 °C·min⁻¹, and then flash-pyrolyzed at 900 °C in NH₃ for 15 min. The obtained nitrogen-doped carbon matrix was labeled as N-C.

Synthesis of the mixture of FeCl₂·4H₂O and N-C: 500 mg of N-C and 18 mg of FeCl₂·4H₂O were weighed and poured into a ZrO₂ crucible with one hundred zirconium-oxide balls of 5 mm diameter. The ZrO₂ crucible was then sealed under air and placed in a planetary ball-miller (Fritsch Pulverisette 7 Premium, Fritsch, Idar-Oberstein, Germany). The powders were milled for 4 cycles of 30 min at 500 rpm milling speed. The resulting catalyst precursor (denoted as Fe1NC, with 1 representing 1 wt% Fe) was then pyrolyzed in Ar for one hour with a ramp rate of 5 °C·min⁻¹ at 200, 400, 600, 800 and 1000 °C (denoted as FeCl₂-NC-T, with T representing the maximum pyrolysis temperature).

Non-contact pyrolysis: 120 mg of N-C and 40 mg of FeCl₂·4H₂O were placed separately in two boats in the furnace and then pyrolyzed in Ar for one hour with a ramp rate of 5 °C·min⁻¹ at 1000 °C (denoted as FeCl₂∖NC-T, with T representing the maximum pyrolysis temperature). In addition, FeAc₂ (35 mg) and α-Fe₂O₃ (16 mg) were also used as Fe precursors and denoted as FeAc₂∖NC-T and Fe₂O₃∖NC-T, respectively. The boat containing the iron compound was located upstream in the Ar flow of the boat containing the N-C powder.

Electrochemical characterization-RDE. The catalyst powders were deposited on a glassy carbon working electrode. Catalyst inks were prepared by dispersing 10 mg of the catalyst powder in a mixture of Millipore water (36.5 μL, 18.2 MΩ cm) and ethanol (300 μL, Sigma-Aldrich, 99.8%), into which 5 wt% Nafion solution (108.5 μL, Sigma-Aldrich) was added as a binder phase. The resulting mixture was sonicated for 60 min, and then an aliquot of 8.8 μL was drop-cast onto the glassy carbon electrode (0.247 cm², Pine instrument), resulting in a loading of 800 μg·cm⁻². The working electrode with the de-

posited catalyst layer was used in a three-electrode cell set-up connected to a bipotentiostat (Biologic SP 300) and rotator (Pine Instruments). A graphite rod and reversible hydrogen electrode (RHE) were used as counter and reference electrodes, respectively. The ORR activity was measured in room-temperature O₂-saturated 0.1 M HClO₄ in a voltammetric scan from 0.05 to 1.05 V vs. RHE with a scan rate of 1 mV·s⁻¹ at a glassy carbon electrode rotation rate of 1600 rpm. The cyclic voltammetry (CV) was carried out between 0.05 to 1.05 V vs. RHE with a scan rate of 20 mV·s⁻¹ in N₂-saturated 0.1 M HClO₄.

Electrochemical characterization-PEMFC. The FeCl₂/NC-1000 catalyst was used to prepare the cathode for MEA tests in a PEMFC under H₂-O₂ conditions, followed by H₂-air test. The cathode catalyst inks were prepared by dispersing calculated amount of catalyst powder and Nafion D521 dispersion (Ion power) into 50 wt/% 1-propanol aqueous solution for 3 hours under ice bath sonication. The inks were coated layer by layer on SGL 29-BC gas diffusion layer (Sigracet) until 4 mg catalyst/cm² loading was achieved. An commercial Pt gas diffusion electrode (0.3 mg_{Pt}·cm⁻², fuel cell store) was used as the anode. The anode electrode was first hot pressed onto NR212 membrane (Ion Power) at 130 °C for 4 minutes. Before hot pressing the cathode on the opposite side of the membrane, a thin Nafion overspray layer was applied on the cathode catalyst layer to reduce the interfacial resistance. The cathode was then hot pressed on the previously-pressed half MEA at 130 °C for 2 minutes. The MEA was then assembled into a single cell with single-serpentine flow channels. The single cell was then evaluated in a fuel cell test station (100 W, Scribner 850e, Scribner Associates). The cells were conditioned under N₂ environment, at 100% relative humidity and 80 °C for at 2hours. Air/oxygen flowing at 1000 ml·min⁻¹ and H₂ (purity 99.999%) flowing at 200 ml·min⁻¹ were used as the cathode and anode reactants, respectively. The back pressures during the fuel cell tests are 1.0 bar reactant gas. The vapor pressure is around 0.5 bar owing to the 100% relative humidity. Thus, the total pressure applied to the MEA is around 1.5 bar (150 KPa). Fuel cell polarization curves were recorded in a voltage control mode.

Physical characterizations.

TEM: Transmission electron microscopy (TEM) images of N-C were taken on a FEI T12 operated at 120 kV at University of California, Los Angeles (UCLA).

SEM: Scanning electron microscopy (SEM) micrographs of N-C were obtained with a Hitachi S-4800 apparatus (Hitachi, Tokyo, Japan).

XRD: X-ray diffraction (XRD) patterns were conducted using a PANanalytical X'Pert Pro powder X-ray diffractometer with Cu K α radiation.

XPS: X-ray photoelectron spectroscopy (XPS) tests were done with Kratos AXIS Ultra DLD spectrometer with Al K α (1486.6 eV) X-ray source at UCLA.

N₂ adsorption/desorption analysis: N₂ sorption analysis was performed at liquid nitrogen temperature (77 K) with a Micromeritics ASAP 2020 instrument. Prior to the measurements, all samples were degassed at 200 °C for 5 h in flowing nitrogen to remove guest molecules or moisture. The pore size distributions were calculated by fitting the full isotherm with the quench solid density functional theory model with slit pore geometry from NovaWin (Quantachrome Instruments).

Mössbauer spectroscopy: ⁵⁷Fe Mössbauer spectroscopy was used to obtain information on iron speciation. Samples of ~300 mg were mounted in a 2 cm² holder. Mössbauer spectra were measured at 5 K in a helium flow cryostat (SHI-850 Series from Janis, USA). The Mössbauer spectrometer (Wissel, Germany) was operated in the transmission mode with a ⁵⁷Co: Rh source at room temperature. The velocity driver was operated in the constant acceleration mode with a triangular velocity waveform. The velocity scale was calibrated with the magnetically split sextet of a high-purity α -Fe foil at room temperature. The spectra were fitted to appropriate combinations of Lorentzian profiles representing quadrupole doublets and sextets by least-squares methods. Isomer shifts are given relative to α -Fe at room temperature.

X-ray fluorescence: the metal contents in the FeNC catalysts obtained from non-contact pyrolysis were measured via X-ray fluorescence (XRF) spectroscopy (Axios Max from PANanalytical, Netherlands). The sample powders were mixed with boric acid as a binder in a ratio of 1:3 by weight *via* ball milling at 400 rpm for 30 min. Then 200 mg of the mixture was pelletized as a disk of 13 mm diameter for XRF measurements. The calibration curve was performed using 0.1, 0.2, 0.5, 1.0, 1.5 and 2.0 wt% Fe in a mixture of FeAc₂ and Vulcan XC72R. The Vulcan XC72R (mixed with FeAc₂) were mixed with boric

acid in a ratio of 1:3 by weight *via* ball milling at 400 rpm for 30 min, and then 200 mg of the mixture was pelletized as a disk of 13 mm diameter. All the XRF measurements were performed under vacuum.

In-temperature XAS measurements. The *in-temperature* XAS measurements during pyrolysis were performed at beamline 10-ID of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory, Lemont, Illinois, United States. The experimental apparatus for these experiments and the results of the first use of the apparatus to study the evolution of the Fe speciation during heat treatment of a Fe-doped ZIFs are described in Myers *et al.*³⁰⁻³²

The powder precursors were loaded into a custom-built holder comprised of alumina tubes with inner diameters of 0.4 cm. A quantity of each powder needed to yield a Fe K-edge edge step of approximately 0.25 to 1 (0.09 to 0.3 mg Fe) was ball-milled for 2 hours for sufficient mixture and then packed into separate alumina tubes in the holder. The alumina tube holders were placed in the center of a quartz tube, equipped with gas and thermocouple ports and Kapton windows. A K-type thermocouple measured the temperature inside the quartz tube and was located just above the alumina tube sample holder. The quartz tube was placed in a clamshell furnace, mounted on a positioning platform. The beam was rastered over the sample holder by manipulating the position of the platform. Once the sample positions were fine-tuned, the quartz tube was purged with approximately 100 sccm flow of 99.995% helium, which had been passed through an oxygen trap. The Fe K-edge spectra were recorded in transmission mode and an iron foil spectrum was measured simultaneously with each sample spectrum for energy calibration. Transmission data was taken from 6.950 keV to 7.942 keV. Spectra were taken at room temperature, then the quartz tube was heated at a ramp rate of approximately 15 °C/min under flowing helium to approximately the following temperature set points during the increasing temperature portion of the temperature profile: room temperature, 300 °C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C. This was followed by controlled cooling to room temperature with temperature set points of 800 °C, 600 °C, 200 °C, and room temperature at which spectra were acquired. Once the samples had cooled to room temperature, the helium flow was stopped, the quartz tube was opened to atmospheric air, and XAS scans were collected. Multiple XAS scans were collected at each temperature set point.

The hold time at each temperature was approximately 15 minutes. The XAS data were processed and fitted using the Ifeffit-based Athena and Artemis programs.³³ Scans were calibrated, aligned, and normalized with background removed using the IFEFFIT suite.³³ The $\chi(R)$ were modeled using single scattering paths calculated by FEFF6.³⁴

The MOF-based mixture was prepared for the *in-temperature* XAS experiments by first combining ZnO, imidazole, ammonia sulfate, and 200 μ L MeOH in a plastic container and ball milling the mixture for one hour using two plastic balls. This was followed by addition of 1,10-phenanthroline and FeAc₂ to the mixture and ball milling for an additional two hours. The amounts of the reactants are summarized in Table S1. The Fe content in the mixture was ~0.3 wt%.

The amounts of FeCl₂·4H₂O used for the *in-temperature* XAS experiments are listed below:

30 mg FeCl₂·4H₂O + 150 mg SiO₂, (~4.6 wt% Fe).

14.4 mg FeCl₂·4H₂O + 400 mg N-doped carbon matrix (~1 wt% Fe).

***Ex situ* XAS measurements.** Fe K-edge XAS was conducted at room temperature at the SAMBA beamline, Synchrotron SOLEIL. The beamline is equipped with a sagittally focusing Si 220 monochromator and two Pd-coated mirrors that were used to remove X-rays harmonics. The catalysts were pelletized as disks of 10 mm diameter with 1 mm thickness using Teflon powder (1 μ m particle size) as a binder.

Results and Discussions

Section 1. N-C Characterizations

Figure S1. (A) SEM, (B) TEM, (C) XRD, (D) N_{1s} XPS spectrum, (E) N_2 physisorption isotherm, and (F) the pore size distribution of N-C.

Section 2. *In-temperature* XAS on the mixture of $FeCl_2 \cdot 4H_2O$ and N-C.

Figure S2. The fitting of the spectrum of $FeCl_2$ -NC-600 in (A) R -space and (B) K -space. S_0^2 was fixed at 0.74 as obtained by fitting the reference foil. Fits were conducted in R -space with $k^{l,2,3}$ weighting, $1.0 < R < 2.1$ Å, and $\Delta k = 2.6 - 9.8$ Å⁻¹. The fit E_0 was -0.3 ± 0.9 eV.

Figure S3. The (A) XANES and (B) first derivative XANES of $\text{FeCl}_2\text{-NC-600}$ and Fe(II)Pc . The presence or absence of the shoulder at ~ 7112 eV of the $\text{FeCl}_2\text{-NC-600}$ and Fe(II)Pc , respectively, reflect the tetrahedral Fe-O_4 versus in-plane Fe-N_4 local structure, respectively.

Figure S4. The corresponding cyclic voltammograms (CV) of $\text{FeCl}_2\text{-NC-T}$ catalysts were obtained in room-temperature Ar-saturated 0.1 M HClO_4 from 0.05 to 1.05 V vs. RHE with a scan rate of $20 \text{ mV} \cdot \text{s}^{-1}$.

1.

Figure S5. The fitting of the spectrum of FeCl₂-NC-1000 in the (A) *R*-space and (B) *K*-space. S_0^2 was fixed at 0.74 as obtained by fitting the reference foil. Fits were conducted in *R*-space with $k^{1,2,3}$ weighting, $1.0 < R < 2.2$ Å, and $\Delta k = 2.3 - 9.7$ Å⁻¹. The fit result for E_0 was -1.1 ± 1.2 eV.

Figure S6. The fitting of the spectrum of FeCl₂-NC-End in the (A) *R*-space and (B) *K*-space. S_0^2 was fixed at 0.74 as obtained by fitting the reference foil. Fits were conducted in *R*-space with $k^{1,2,3}$ weighting, $1.0 < R < 2.2$ Å, and $\Delta k = 2.3 - 9.7$ Å⁻¹. The fit E_0 was -0.2 ± 1.5 eV.

Figure S7. The X-ray diffraction patterns of N-C, and the mixture of FeCl₂·4H₂O and N-C pyrolyzed at a variety of maximum temperature. The small peaks observed at 800 °C arise from silica impurities.

Table S2. Summaries of EXAFS fitting results of the first-shell Fe-N/O bonds of FeCl₂-NC based catalysts during the pyrolysis and cooling.

	R (Å)	N	$\sigma^2 \times 10^{-3}$ (Å)	E ₀ (eV)
FeCl ₂ -NC-600	1.99±0.01	3.6±0.4	17±2	-0.3±0.9
FeCl ₂ -NC-1000	1.92±0.01	4.5±0.7	12±2	-1.1 ± 1.2
FeCl ₂ -NC-RT	1.91±0.01	4.3±0.4	7±2	-0.2±1.5

S_0^2 was fixed at 0.74 as obtained by fitting the reference foil.

Table S3. Parameters obtained from fitting the Mössbauer spectrum of FeCl₂-NC-1000 taken at 5 K (**Figure 1D**): relative area (RA, %), isomer shift (IS, mm s⁻¹), quadrupole splitting (QS, mm s⁻¹), and line width (LW, mm s⁻¹) of each component.

Comp.	RA %	IS mm s ⁻¹	QS mm s ⁻¹	LW mm s ⁻¹	Assignment
Doublet 1	67	0.46	1.21	0.94	Fe _i (III)-N ₄ -O ₂
Doublet 2	33	0.65	2.79	1.31	Fe _i (II)-N ₄

Section 3. *In-temperature* XAS on the mixture of MOF-based mixture.

The XANES spectrum of the mixture of Fe(II)Ac₂, 1,10-phenanthroline monohydrate, and ZIF-8 subjected to ball milling prior to pyrolysis is about 4 eV positive to that of the pristine Fe(II)Ac₂, close to that of the α -Fe₂O₃ standard (Figure S8A). The associated FT-EXAFS of the mixture at room temperature (Fe-MOF-RT) exhibits a prominent peak around 1.5 Å (all the FT-EXAFS peak positions reported here are without phase correction and ~0.5 Å smaller than the corresponding bond lengths) and a short peak around 2.8 Å (Figure S8B). These two peaks overlap those of α -Fe₂O₃, but the Fe-Fe peak around 2.8 Å has a much lower intensity (Figure S8B), indicating the presence of Fe vacancies. The FT-EXAFS Fe-Fe peaks of Fe-MOF-RT at 2.4 Å and 2.8 Å in real and imaginary spaces nicely overlap those of α -Fe₂O₃, but not that of the Fe(II)Ac₂ exposed to air (Figure S9A and S9B), which excludes the oxidized Fe(II)Ac₂ as the major Fe species upon ball milling. These two peaks are in association with the Fe-Fe bond within the octahedral layer with a bond length of 2.9 Å and that between octahedral layers with a

bond length of 3.4 Å, respectively, in α -Fe₂O₃.^{35, 36} The first shell EXAFS fitting (Figure S8D) gives a Fe-O coordination number of 6.0 ± 0.4 , and an average Fe-O bond length of 1.98 ± 0.01 Å (Table S3), comparable to those of α -Fe₂O₃.^{35, 36} These results together confirm the partial transformation of Fe(II)Ac₂ to ferric oxides with deficient Fe-Fe bonds upon ball milling.

Figure S8. The thermal evolution of (A) XANES, (B) FT-EXAFS, and (C) first derivative XANES of the Fe-MOF mixture along with temperature increase from room temperature to 1000 °C and cooling to room temperature. The vertical line is to guide the eye. (D) The fitting of the Fe-MOF mixture at room

temperature prior to pyrolysis in the R -space. S_0^2 was fixed at 0.74 as obtained by fitting the reference foil. Fits were done in R -space, $k^{1,2,3}$ weighting. $1.0 < R < 2.2 \text{ \AA}$ and $\Delta k = 2.2 - 12.8 \text{ \AA}^{-1}$ were used. The fitting result of the E_0 is $0.2 \pm 0.8 \text{ eV}$.

The ferric oxides are largely reduced to ferrous oxides at 300°C as signified by the negative shift of the XANES spectra of $\sim 4 \text{ eV}$, nicely overlapping that of the pristine Fe(II)Ac_2 (Figure S8A). While the pristine Fe(II)Ac_2 exhibits only one Fe-Fe peak around $2.8 \text{ \AA}$ (Figure S8B) in association with a Fe-Fe bond length of $3.3 \text{ \AA}$,³⁶ the Fe-Fe peak of Fe-MOF-300 at $2.8 \text{ \AA}$ largely diminish and the peak around $2.4 \text{ \AA}$ becomes prominent, excluding the formation of Fe(II)Ac_2 as the major Fe species at 300°C . A closer examination of the FT-EXAFS of Fe-MOF-300 reveals that the Fe-O peak around $1.5 \text{ \AA}$ and the Fe-Fe peaks around $2.4 \text{ \AA}$ and $2.8 \text{ \AA}$ overlap those of the Fe(II)O standard in both the real and imaginary spaces, and the Fe-Fe peak at $2.8 \text{ \AA}$ becomes barely discernible (Figure S9C and S9D). The selective disappearance of the long Fe-Fe bonds between octahedral layers suggests the formation of 2-dimensional ferrous oxides. These results indicate the 3-dimensional ferric oxides with a local structure of octahedral Fe-O_6 transform to 2-dimensional ferrous oxides with Fe vacancies ($\text{Fe}_{1-x}(\text{II})\text{O}$) under an oxygen deficient environment, in agreement with the Fe-O phase diagram.^{26, 27}

Figure S9. The FT-EXAFS of Fe-MOF-RT in (A) real space and (B) imaginary space, in comparison with that of the Fe(II)Ac₂ exposed to air and α -Fe₂O₃; and of the Fe-MOF-300 in (C) real space and (D) imaginary space, in comparison with that of the Fe(II)Ac₂ and Fe(II)O.

As the temperature gradually increases to 600 °C, the XANES main peak intensity significantly decreases, whereas the $1s \rightarrow 3d$ transition feature at 7112 eV becomes more intense (Figure S8A), which indicates that the local structure of the octahedral Fe-O₆ in Fe_{1-x}(II)O transforms to a more closely packed tetrahedral Fe₁(II)-O₄.^{23, 37} The reduced coordination number of Fe-O and shortened Fe-O bond length expected from this transformation are evidenced by the reduced intensity of the Fe-O peak at ~ 1.5 Å and its shift to lower R values (Figure S8B), respectively. The reduced Fe-Fe peak intensity indicates that this transformation is associated with the breaking of the Fe-Fe bonds. This crystal-to-melt-like transformation from the Fe-O₆ with Fe-Fe bonds to Fe₁(II)-O₄ without Fe-Fe bonds observed between 300-600 °C coincides well with that observed during pyrolysis of the FeCl₂·4H₂O and N-C mixture.

Starting from 600 °C, the $1s \rightarrow 4p_z$ transition XANES feature around 7117 eV, which is the fingerprint of the in-plane $\text{Fe}_1(\text{II})\text{-N}_4$ structure^{12, 13, 38} emerges in the first derivative of XANES (Figure S8C). The formation of the in-plane $\text{Fe}_1(\text{II})\text{-N}_4$ is further supported by the splitting of the scattering peak around 1.5 Å into two peaks at 700 °C, which indicates the co-existence of two Fe compounds with different bond length. Meanwhile, the diminishing of the Fe-Fe peak at 700 °C suggests the absence of the Fe-Fe bonds in both tetrahedral $\text{Fe}_1(\text{II})\text{-O}_4$ and in-plane $\text{Fe}_1(\text{II})\text{-N}_4$ moieties (Figure S8B). As the temperature further increases to 1000 °C, the XANES remains largely unchanged, while the FT-EXAFS peak switches back to one peak that overlaps the Fe-N peak of FePc, but negative to the Fe-O peak present at low temperatures (Figure S8B). The EXAFS spectrum collected at 1000 °C (Fe-MOF-1000) can be well fitted with a Fe-N₄ model (Figure S10) with a first shell Fe-N coordination number of 3.7 ± 0.5 and bond length of 1.94 ± 0.01 Å (Table S3) that is close to that of FePc (1.93 Å),³⁹ quantitatively confirming the formation of in-plane $\text{Fe}_1(\text{II})\text{-N}_4$. Collectively, these results reveal the thermal evolution process as: $\text{FeAc}_2 \rightarrow \text{ferric oxides (octahedral Fe-O}_6) \rightarrow \text{Fe(II)}_{1-x}\text{O} \rightarrow \text{tetrahedral Fe}_1(\text{II})\text{-O}_4 \rightarrow \text{in-plane Fe}_1(\text{II})\text{-N}_4$, essentially the same as that observed for the mixture of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and N-C (Figure 2C).

Figure S10. The fitting of the spectrum of Fe-MOF-1000 in (A) R -space and (B) K -space. S_0^2 was fixed at 0.74 as obtained by fitting the reference foil. Fits were conducted in R -space, with $k^{1,2,3}$ weighting, $1.0 < R < 2.2$ Å, and $\Delta k = 2.3 - 10.1$ Å⁻¹. E_0 was fit at -0.2 ± 1.5 eV.

Table S4. Summaries of EXAFS fitting results for the Fe-MOF-based precursor before pyrolysis (Fe-MOF-RT) and at the maximum pyrolysis temperature (Fe-MOF-1000).

	Bond	R (Å)	N	$\sigma^2 \times 10^{-3}$ (Å ²)	E ₀ (eV)
Fe-MOF-RT	Fe-O	1.98±0.01	6.0±0.8	10±2	0.1±1.0
Fe-MOF-1000	Fe-O	1.94±0.01	3.7±0.5	13±3	-1.8±1.8

* S_0^2 was fixed at 0.74 as obtained by fitting the reference foil.

Section 4. *In-temperature* XAS on the mixture of FeCl₂·4H₂O and SiO₂.

Nanoscale SiO₂ powder free of N and C was deliberately chosen here to dilute the FeCl₂·4H₂O powders for XAS measurements due to the high thermal stability and low absorption cross-section over the energy range of the XAS measurements. The mixture at room temperature exhibits a typical FT-EXAFS Fe-O (O from H₂O) peak at 1.5 Å and an Fe-Cl peak at 2.0 Å (Figure S11A). The lower intensity of the Fe-O peak in the mixture compared to that of FeCl₂·4H₂O indicates the detachment of H₂O molecules during ball milling. The disappearance of the Fe-O peak at 300 °C shows a complete loss of H₂O molecules at this temperature (Figure S11A). The Fe-Cl peak gradually diminishes as the temperature increases to 600 °C, accompanied by the emergence of an Fe-O peak at 1.4 Å, but not Fe-Fe peaks. The fitting of the EXAFS spectrum at 600 °C (FeCl₂-SiO₂-600) (Figure S12) gives an Fe-O coordination number of 3.9 ± 0.6 and a bond length of 2.00 ± 0.02 Å (Table S4), which are close to those of the FeCl₂-NC-600 (Table S2) and the tetrahedral Fe₁(II)-O₄ structure reported previously.²³ This quantitatively confirms the formation of tetrahedral Fe₁(II)-O₄ moieties in FeCl₂-SiO₂-600. More importantly, it supports the assignment of the FeCl₂-NC-600 path with a bond distance of 1.99 ± 0.01 Å and a coordination number of 3.6 ± 0.4 to Fe-O bond rather than Fe-N or Fe-C.

Figure S11. The evolution of the (A) FT-EXAFS and (B) XANES of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ mixed with SiO_2 during the temperature ramp from room temperature to 1000 °C. The vertical solid lines in (B) are guides for the eye. The comparison of the (C) FT-EXAFS in real space of $\text{FeCl}_2\text{-SiO}_2\text{-600}$, $\text{FeCl}_2\text{-SiO}_2\text{-700}$, and Fe(II)O and (D) XANES of $\text{FeCl}_2\text{-SiO}_2\text{-600}$ and $\text{FeCl}_2\text{-SiO}_2\text{-700}$.

Figure S12. The (A) K-space XAFS and FT-EXAFS in (B) R space, (C) real space, and (D) imaginary space of the $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ mixed with SiO_2 ($\text{FeCl}_2\text{-SiO}_2\text{-600}$) or with N-C ($\text{FeCl}_2\text{-NC-600}$) at 600 °C during the increasing temperature ramp.

Figure S13. The fitting of the spectrum of $\text{FeCl}_2\text{-SiO}_2\text{-600}$ EXAFS in (A) R-space and (B) K-space. S_0^2 was fixed at 0.74 as obtained by fitting the reference foil. Fits were done in R-space, with $k^{l,2,3}$ weighting, $1.0 < R < 2.2$ Å, and $\Delta k = 2.3 - 10.1$ Å⁻¹. E_0 was fit at 0.9 ± 1.6 eV.

As the temperature increases from 600 °C to 700 °C, an Fe-Fe peak at 2.4 Å, observed in Fe_{1-x}(II)O in Figure S8B, emerges (Figure S11A). The Fe-O and Fe-Fe peaks shift to larger R values overlapping those of Fe(II)O (Figure S11C). Meanwhile, the 1s → 3d transition XANES feature at 7112 eV becomes less intense, the edge energy shifts to higher values, and the intensity of the major XANES peak increases dramatically (Figure S11D). These results indicate a transformation from the tetrahedral Fe₁(II)-O₄ to ferrous oxides with a local structure of octahedral Fe-O₆, akin to the melt-to-crystal transition process. As the temperature further increases to 1000 °C, the intensities of both the Fe-O and Fe-Fe peaks reduce, and the Fe-Fe peak shifts negatively from 2.4 Å to 2.1 Å, overlapping the first shell Fe-Fe peak of the Fe foil (Figure S11A). Correspondingly, the intensity of the primary XANES peak drops substantially (Figure S11B). These trends verify the reduction of Fe_{1-x}(II)O to Fe nanoparticles with the oxygen neighbors removed. If this also occurs on the co-existing Fe₁(II)-O₄ without Fe-Fe bonds, Fe₁ may form.

Table S5. Summaries of EXAFS fitting results for FeCl₂-SiO₂-600.*

	R (Å)	N	$\sigma^2 \times 10^{-3}$ (Å ²)	E ₀ (eV)
FeCl ₂ -SiO ₂ -600	2.00±0.02	3.9±0.6	19±5	0.5±2

*S₀² was fixed at 0.74 as obtained by fitting the reference foil.

Section 5. Non-contact pyrolysis of three different Fe precursors.

Figure S14. The X-ray diffraction patterns of the three indicated catalysts obtained by non-contact pyrolysis, as well as the N-C substrate. Note the sharper carbon peak around 27 degrees for FeCl₂/NC-1000

and FeAc₂/NC-1000 compared to that of Fe₂O₃/NC-1000 as a consequence of the Fe-induced graphitization.

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