

Impacts of Imidazolate Ligand on Performance of Zeolitic-Imidazolate **Framework-Derived Oxygen Reduction** Catalysts

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Supporting Information

ABSTRACT: Carbon-hosted Fe-N-coordinated (Fe/N/C) materials, especially those derived from thermolysis of iron-added zinc-based zeoliteimidazolate frameworks (ZIFs), have emerged as the most promising platinum group metal-free (PGM-free) oxygen reduction reaction (ORR) catalysts. However, the impacts of the precursory ZIF structure and their conversion chemistry during thermal activation to the final catalytic activity remain to be further explored in the process of continuously refining the catalyst performance. Herein, we synthesized a series of Fe-doped ZIFs with different imidazolate ligands and systematically studied the correlation between the crystal structures with the final ORR catalytic activity in an alkaline electrolyte. We also investigated the ZIF decomposition chemistry during pyrolysis using a thermogravimetric mass-spectroscopic analysis. We demonstrated that imidazole side-chain substitution alters the ZIF's



decomposition during pyrolysis, influencing the elemental compositions, surface properties, graphitization levels, and ultimately the catalytic performance. The $Zn(mIm)_2$ TPIBP catalyst affords the highest ORR activity with a half-wave potential of 0.93 V vs RHE, representing the best among all PGM-free catalysts studied.

nvironmentally friendly, all electric vehicles (EVs) have recently garnered much attention because of worldwide concerns regarding fossil fuel consumption and emission from internal combustion engine vehicles.¹ One of the most promising EVs is the hydrogen-powered fuel cell with the advantage of long cruising range and short refueling time.² Fuel cell commercialization relies on the cost reduction, of which reducing or removing platinum group metal (PGM) usage in the electrocatalysts represents a particularly important path.³ Compared to the anode, the cathodic oxygen reduction reaction (ORR) has significantly higher kinetic barrier and requires more PGM catalysts. If PGMs can be replaced by earth-abundant elements with a simple synthetic route, the fuel cell cost will then be substantially lowered.⁴ Exploration of transition metal/ nitrogen coordinated carbon (TM/N/C) as an ORR catalyst was initiated by Jasinski in 1964 using Co phthalocyanine as precursors.⁵ Ever since, the research in this direction has attracted a great following. In particular, Fe/N/C catalysts have

received a significant amount of attention in recent years because of their promising catalytic activity.^{6–10}

Ideally, an effective ORR catalyst should have high volumetric active site density exposed by high surface area without inactive support such as amorphous carbon used in the traditional electrocatalyst. Using metal-organic frameworks (MOFs), such as zeolitic imidazolate frameworks (ZIFs), as the precursors exemplifies such an approach. Since the original studies of ZIFbased PGM-free ORR catalysts,^{6,11} studies on ZIFs as catalytic precursors have undergone a rapid expansion with many promising results,¹² particularly for Fe/N/C catalysts prepared from ZIFs containing coordinated^{13–15} or added iron.^{16–18} As the precursors, ZIFs are attractive because of their tunable structure, inherent porosity, high surface area, and diverse

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Figure 1. (a) Ligation structure for tris(1,10-phenanthroline) iron(II) perchlorate (TPI) and Zn-ligand coordination structures in (b) $Zn(MIm)_{2'}$ (c) $Zn(eIm)_{2'}$ (d) $Zn(4abIm)_{2'}$ and (e) $Zn(Im)_{2}$. Black, carbon; blue, nitrogen; red, iron; and green, zinc.



Figure 2. RRDE results from (A) ORR linear sweep voltammetry polarization curve, (B) Tafel plot of mass-corrected kinetic current, and (C) the number of electrons transferred as the function of polarization potential. (D) Percentage loss of kinetic current density against the initial value measured at 0.90 V (vs RHE) as a function of voltage cycle.

composition, all originating from the ordered 3D framework formed by repetitive $M-N_4$ ligations.¹⁹ Upon carefully controlled heat-treatment, Fe-containing ZIFs can be converted into a highly porous carbonaceous ORR catalyst uniformly decorated by Fe/N/C active sites.

In the ZIF structure, the imidazole ligand controls the porosity, surface area, and topology.^{20,21} During the thermal

conversion, one expects that a majority of the pentagonal imidazolate rings will be transformed to hexagonal graphitic structure through decomposition and rearrangement.¹¹ The side functional group of the imidazolate will participate and influence the conversion pathway and consequently the final catalyst porosity and surface functionality. Although significant progress has been made in improving the ORR performance, the

influence of the ZIF ligand on catalyst activity has been explored only by a limited yet insightful investigation.²²

Herein, we prepared four ZIF-derived catalysts using our previously demonstrated one-pot ZIF synthesis method¹⁶ and systematically investigated their ORR activities in alkaline media. Four ZIFs were prepared through the solid-state reaction between ZnO with imidazole (HIm), 2-methylimidazole (HmIm), 2-ethylimidazole (HeIm), or 4-azabenzimidazole (H4abIm). Tris (1,10-phenanthroline)iron(II) perchlorate (TPI) was added to incorporate both iron and ligated nitrogen into the precursors. ZIFs with imidazole of different side chains are denoted as Zn(ligand)₂. The coordination structures of TPI, $Zn(Im)_{2}$, $Zn(mIm)_{2}$, $Zn(eIm)_{2}$, and $Zn(4abIm)_{2}$ are given in Figure 1. Samples containing TPI are denoted as Zn-(ligand)₂TPI and, after ball-mill, Zn(ligand)₂TPIB. The resulting powder samples were subject to pyrolysis to produce the final catalysts, denoted as Zn(ligand)₂TPIBP. Elemental analysis showed these catalysts contain a similar amount of Fe at ca. 1 wt % (Table S1). To better understand the ZIF-to-catalyst conversion process, we further investigated the catalyst structure as a function of the ligand and the pyrolysis chemistry. The results demonstrated that the imidazolate ligand in ZIF impacts strongly on the final catalyst's surface property and composition. The catalyst derived from Zn(mIm)₂TPIBP showed the best ORR catalytic activity, correlated to its higher surface area and pyridinic-N content. Detailed procedures on the catalyst synthesis can be found in the Supporting Information.

The catalytic activity and durability were tested using RRDE methods in an alkaline solution (0.1 M KOH). All the potentials reported are in reference to the reversible hydrogen electrode (RHE). Figure 2A displays linear sweep voltammograms (LSVs) of all four catalysts. The onset potentials (E_0) in Table 1 were

Table 1. Onset Potential (E_0) , Half-Wave Potential $(E_{1/2})$, Mass-Corrected Kinetic Current (I_{mK}) at 0.90 V (vs. RHE), and Tafel Slope for All Four PGM-Free Electrocatalysts

electrocatalyst	$\begin{bmatrix} E_0 \\ V \text{ vs RHE} \end{bmatrix}$	E _{1/2} [V vs RHE]	$\stackrel{I_{\rm mK}}{[{\rm A}{\cdot}{\rm g}^{-1}]}$	Tafel slope [mV·dec ⁻¹]
$Zn(mIm)_2TPIBP$	1.14	0.93	18.89	89
$Zn(eIm)_2TPIBP$	1.12	0.92	10.62	98
$Zn(4abIm)_2TPIBP$	1.12	0.90	7.46	95
$Zn(Im)_2TPIBP$	1.11	0.86	2.97	124

measured from the LSVs at the current density of 22 μ A·cm⁻². Additionally, half-wave potentials $(E_{1/2})$ were recorded at the half point between onset and diffusion-limited current densities and are also listed in Table 1. A commercial Pt/C catalyst was also tested as a reference with optimized E_0 of 1.05 V and $E_{1/2}$ of 0.88 V at the platinum loading of 60 μ g_{Pt}·cm⁻² (Figures S1A and Figure S2). For PGM-free catalysts, Zn(mIm)₂TPIBP exhibited an E_0 of 1.14 V and an $E_{1/2}$ of 0.93 V, representing the best ORR catalytic activity for a PGM-free catalyst in the alkaline electrolyte according to the literature (Table S2). Zn-(eIm)₂TPIBP and Zn(4abIm)₂TPIBP also displayed excellent activities with $E_{1/2}$ of 0.92 and 0.90 V, respectively. All three catalysts surpassed the Pt/C benchmark in E_0 and $E_{1/2}$. $Zn(Im)_2TPIBP$, the catalyst derived from imidazolate without side chain, showed a lower activity with an E_0 of 1.11 V and an $E_{1/2}$ of 0.86 V.

To assess the ORR reaction kinetics, the mass-corrected kinetic current (I_{mK}) of the PGM-free catalysts was calculated at 0.90 V and is listed in Table 1. Among the PGM-free catalysts,

Zn(mIm)₂TPIBP has the highest I_{mK} of 18.89A·g⁻¹; Zn-(eIm)₂TPIBP and Zn(4abIm)₂TPIBP also possess excellent I_{mK} of 10.62 and 7.46 A·g⁻¹, respectively, whereas Zn-(Im)₂TPIBP underperforms. The RRDE Tafel plots are shown in Figure 2B, of which the slope characterizes the ORR kinetics. Zn(mIm)₂TPIBP afforded a Tafel slope as low as 89 mV·dec⁻¹ at low overpotentials, indicating a faster current surge with the increase of polarization potential, similar to that of Pt/C (Figure S1B). We also estimated the ORR turnover frequency (TOF) at 0.90 V (vs RHE) over Zn(mIm)₂TPIBP by assuming all Fe sites were atomically dispersed.²³ The TOF was found to be 0.21 s⁻¹·atom⁻¹ for Zn(mIm)₂TPIBP, which is in general agreement with those reported in the literature (Supporting Information).

The RRDE method was also used to measure the number of electrons transferred, *n*, at different polarization potential drawn from the disk and ring currents (Figure 2C). As n = 4 represents the complete conversion of oxygen to water ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$), lower electron-transfer numbers are the result of the formation of 2e⁻ intermediate H_2O_2 . Hydrogen peroxide can corrode the PGM-free catalysts and ion-conductive membrane in the fuel cell and therefore should be minimized. Zn-(mIm)₂TPIBP achieved excellent *n* values, ranging from 3.94 to 3.99 within the polarization potential range. Zn(eIm)₂TPIBP and Zn(4abIm)₂TPIBP also showed good *n* values ranging from 3.90 to 3.99 and 3.86 to 3.99, respectively. At the preferred fuel cell operating voltage >0.7 V, all the catalysts displayed $n \approx 4$ and low H_2O_2 production, except for Zn(Im)₂TPIBP (Figure S3).

The durability of the PGM-free catalysts was evaluated under repeated potential cycling from 0 to 1.20 V in O₂-saturated 0.1 M KOH (Figures S4 and S5). LSVs were recorded after a designated number of cycles, and the kinetic current densities (j_K) at 0.90 V were measured and normalized against that of the fresh catalyst (Figure 2D). The retention of j_K after 10 000 cycles follows the order of Zn(Im)₂TPIBP (73.4%) > Zn(eIm)₂TPIBP (71.8%) > Zn(mIm)₂TPIBP (66.8%) > Zn(4abIm)₂TPIBP (61.5%). The catalyst with the lowest activity, Zn(Im)₂TPIBP, exhibited the highest durability, while the others showed similar deactivation rates.

Our study suggests that the structure of the imidazole ligand in ZIF influences the ORR activity and durability of the final catalyst. The catalyst with the best ORR activity is from ZIF with the 2-methylimidazolate ligand. The activity decreases only slightly with higher alkyl side-chain substitution, as are the cases for 2-ethylimidazolate and 4-azabenzimidazolate, but Zn-(eIm)₂TPIBP showed better durability than Zn(mIm)₂TPIBP. The imidazolate ligand without the side chain leads to the lowest activity for Zn(Im)₂TPIBP. The ligand size affects the composition, structure, and graphitization level, all of which affect the catalyst's activity and durability. As we will discuss below, these catalyst properties are influenced by liganddetermined ZIF surface property and decomposition chemistry.

The catalysts were characterized by a variety of techniques. Xray diffraction (XRD) patterns of catalysts after synthesis and ball milling to NH₃ activation were also included in Figure S6, compared to simulated XRD patterns.^{20,24} The addition of the iron complex did not alter the crystalline structure of ZIFs because TPI remains outside the ZIF cavity as the result of its large size. After ball milling, Zn(mIm)₂TPIB exhibited extensive peak broadening due to the loss of long-range crystal ordering.^{25,26} In contrast, Zn(Im)₂TPIB, Zn(eIm)₂TPIB, and Zn(4abIm)₂TPIB showed only minor peak broadening, attributed to their lattice rigidity in the absence of porosity.



Figure 3. (A) Relative pyridinic-N content and BET specific surface area (SSA) plotted as a function of mass-corrected kinetic current density at 0.90 V (vs RHE). (B) Diffusion-limited current density at 0.60 V (vs RHE) plotted as a function of BET SSA. (C) Tafel slope and half-wave potential $(E_{1/2})$ plotted as a function of micropore volume. (D) Relationship between the durability and graphitization level of the catalysts.

After thermal activation, no crystallinity was found in all catalysts except $Zn(Im)_2TPIBP$, which displayed a graphite crystallite feature. Figure S7 shows the Raman spectra of the catalysts. The spectra between 800 and 2000 cm⁻¹ can be fitted into four peaks, two of which represent defect-activated (D band, 1347 cm⁻¹) and planar motion of sp²-carbon atoms (G band, 1593 cm⁻¹).²⁷ The intensity ratio of these two bands, I_G/I_D , characterizes the catalyst graphitization level with higher value being more graphitized. We found that this ratio follows $Zn(Im)_2TPIBP$ (0.53) > $Zn(eIm)_2TPIBP$ (0.52) > $Zn(mIm)_2TPIBP$ (0.51) > $Zn(4abIm)_2TPIBP$ (0.46), suggesting a decreasing order of the graphitization. Increasing the sizes of imidazole alkyl substitution clearly led to more amorphous catalyst (Table S3).

The investigations on the catalyst surface properties revealed that Zn(mIm)₂TPIBP has the highest Brunauer-Emmett-Teller (BET) specific surface area (SSA) of 1139 m²·g⁻¹ among the four (Figure S8 and Table S4). The total pore volume follows the same order as the surface area with Zn(mIm)₂TPIBP being the highest (0.62 $\text{cm}^3 \cdot \text{g}^{-1})$ and $\text{Zn}(\text{Im})_2\text{TPIBP}$ the lowest $(0.30 \text{ cm}^3 \cdot \text{g}^{-1})$. The catalysts' morphology and composition were also studied by transmission electron microscopy (TEM), showing a uniform and porous $Zn(mIm)_2$ TPIBP in the absence of agglomerated metal particles (Figure S9A,B). The elemental mapping of Fe and N showed that they are both populated densely and uniformly within the carbon matrix (Figure S9C-E). TEM images also found that Zn(eIm)₂TPIBP and Zn(4abIm)₂TPIBP (Figure S10A,B) are significantly more amorphous than Zn(Im)₂TPIBP, of which the graphitic carbons such as nanotubes and iron carbide particles were detected (Figure S11). $Zn(mIm)_2$ TPIBP was found to be more porous with less Zn compared to $Zn(eIm)_2$ TPIBP after the same treatment (Figure S12), suggesting that the more porous ZIF precursor leads to more complete Zn elimination and higher porosity in final catalyst.

A number of studies attributed the ORR active site in the Fe/ N/C composite to a single iron atom ligated by four pyridinic or pyrrolic nitrogens embedded on the graphitic surface, $Fe/N_{4}/$ C.^{23,28} The empirical connection between the catalyst chemical/ structural properties and its performance could shed light on the key descriptors of the active center. To this end, we first studied different nitrogen and carbon moieties in our ZIF-derived catalysts using X-ray photoelectron spectroscopy (XPS) (Figures S13–S15) and tabulated their relative concentrations (Tables S5 and S6). We then examined the correlation between these compositions with the ORR polarization curve at both the kinetic-controlled region (high voltage) and a diffusioncontrolled region (high current). As the descriptors for ORR kinetics, both E_0 and i_K at 0.90 V (vs RHE) increase linearly as the pyridinic-N density increases (Figure 3A), whereas they correlate weakly, if at all, with the pyrrolic-N and graphitic-N contents (Figure S16). This observation is in good agreement with the previous reports on pyridinic-N in promoting the ORR activity more than other N forms.^{29–35} The amount of each N moiety as the function of the total oxidized carbons $(C_x O_y)$ is also plotted (Figure S17). Only pyridinic-N showed a positive correlation with $C_x O_y$, which is consistent with the report by Artyushkova et al.³⁶ on formation of pyridinic-N by carbon oxidation. Figure 3B shows a linear dependence of the oxygen



Figure 4. (A) TGA curves of all PGM-free catalysts, ramping from room temperature to 1000 °C in Ar atmosphere. Mass spectra recorded at (B) mass = 2 (H₂); (C) mass = 15 (methyl); (D) mass = 17 (NH₃); (E) mass = 28 (N₂, CH₂=CH₂), with inset mass = 27 (·CH=CH₂); and (F) mass = 29 (·CH₂-CH₃). Square, Zn(mIm)₂TPIBP; circle, Zn(eIm)₂TPIBP; up-triangle, Zn(4abIm)₂TPIBP; down-triangle, Zn(Im)₂TPIBP.

diffusion-limited current density (j_D) at 0.60 V (vs RHE) on the BET SSA. Because our catalysts are uniform without the distinction between the catalytic and the support surfaces, the higher surface area affords a greater number of exposed Ncontaining active sites and, consequently, a higher current density. Figure 3C indicates that micropore volume has a negative relationship with Tafel slope and a positive relationship with $E_{1/2}$, respectively. This figure indicates two important implications of microporosity for ORR kinetics. Because micropores dominate the majority fraction of the total pore volume and hence the SSA in ZIF-derived catalysts,¹⁶ higher micropore volume provides more exposed active sites therefore higher kinetic current and lower Tafel slope under the same amount of catalyst, for the similar reason described for the limiting current study in Figure 3B. Half-wave potential $E_{1/2}$ is associated with both reaction barrier (E_0) and oxygen transport. The catalyst with higher micropore volume will entrap and concentrate more solvated O₂₁ leading to lower reaction barrier and upshift of $E_{1/2}$ as well as E_0 (Table 1). Figure 3D reveals the positive correlation between the catalyst durability and its graphitization level. Higher carbonization leads to less amorphous catalyst of lower SSA (Figure S18), which tends to be more stable but less active (Figure 3B,C). The Fe/N₄/C type ORR catalyst is prone to deactivation in the acidic media from the demetalation and peroxide oxidation.³⁷⁻³⁹ The former is prompted by the proton binding to the carbonaceous nitrogen leading to deligation of iron, and the latter is caused by the oxidation of the catalyst framework by peroxide formed during ORR. In the alkaline medium, demetalation becomes a lesser issue because of high pH. Oxidative corrosion by the peroxide, on the other hand, becomes an overriding cause. Attack by peroxide is more prevalent on the amorphous region, such as at the edge of the graphene plane. The retention of the ORR activity after 10 000 voltage cycles shown in Figure 3D suggests

that higher $I_{\rm G}/I_{\rm D}$ ratio, or higher graphitization, led to better catalyst durability at the expense of lower surface area. Therefore, the rational design and processing of the Fe/N/C composite require a trade-off between SSA and graphitization.

To better understand the impact of imidazolate ligands on the surface and catalytic properties during thermal activation, we investigated the pyrolysis chemistry of the four ZIFs using thermogravimetric analysis (TGA) in Ar atmosphere coupled with mass spectroscopy (MS). ZIFs, particularly Zn(mIm)₂, are now frequently used in preparing various porous electrochemical and electrocatalytic materials through thermolysis.¹² However, little is known about the chemistry of ZIF ligand-tocarbon transformation under the elevated temperature. Probing decomposition products during the thermolysis could reveal the conversion chemistry and guide the catalyst optimization process. Figure 4A shows the weight loss of all four ZIFs as the function of pyrolysis temperature. The weight-loss of $Zn(eIm)_2TPIB$ starts at the lowest temperature ca. 500 °C, suggesting it as the least stable among the four. Multiple mass fragments were detected simultaneously, indicating several conversion reactions occurring at the same time (Figure 4B-F). For example, hydrogen (mass = 2, Figure 4B) produced from dehydrogenation reaction, starting just below 500 °C and completing slightly above 800 °C, was detected on all four samples, as is expected during the organics-to-carbon conversion. C1 groups such as methyl (mass = 15, Figure 4C) and methane (mass = 16, Figure S19A) were found from Zn(eIm)₂TPIB (560 °C); Zn(mIm)₂TPIB (600 °C); and, to much lesser degree, Zn(Im)₂TPIB (650 °C). These groups were most likely formed from the breaking of the methyl group in $Zn(mIm)_2TPIB$ or C-C bond of the ethyl group in $Zn(eIm)_2$ TPIB. Because ethyl C–C bond breaking can lead to rearrangement of α carbon with imidazolate to form a more stable 6-member ring in the graphitic plane, the process should be more facile and therefore contributes to the higher methyl production by $Zn(eIm)_2TPIB$ over $Zn(mIm)_2TPIB$. A small amount of methyl fragments from $Zn(Im)_2TPIB$ can be generated only from decomposition of imidazole ring because of its lack of side chain. No methyl was detected from $Zn(4abIm)_2TPIB$, suggesting that the imidazole is stabilized by the adjacent azabenzyl group. Similarly, C2 alkyl group such as $\cdot CH_2 - CH_3$ (mass = 29) (Figure 4F) or C_2H_2 (mass = 26) (Figure S19B) were also detected, with $Zn(eIm)_2TPIB$ being the most dominating contributor at lower temperature among all four samples. This can be attributed to detachment of the ethyl group from imidazolate during pyrolysis. Note that both C1 and C2 productions are within a relatively narrow temperature window between 500 °C to 700 °C.

In addition to C1 and C2 groups, we also observed higher molecular weight fragments during pyrolysis. For example, we detected the fragments of mass = 44 at temperature above 550 °C, which can be attributed to C_3H_8 (Figure S19C). This fragment showed the highest intensity from Zn(Im)₂TPIB compared to other samples. Its emission intensity and temperature patterns match well with that of N₂ fragment (discussed below), suggesting a concerted decomposition of the imidazolate ring through which formation of dinitrogen triggers the coproduction of propane. Because imidazolate in Zn-(Im)₂TPIB does not have any sacrificial side chain, the decomposition causes the complete fragmentation of the aromatic ring to smaller hydrocarbon pieces, which subsequently reassimilate into the carbon with higher graphitization level and less nitrogen content. This explains why we observed a higher $I_{\rm G}/I_{\rm D}$ ratio and the highly graphitized carbon species such as carbon nanotubes in pyrolyzed $Zn(Im)_2$ TPIB than in others. Another important fact of higher molecular fragmentation is that the process continued with the rise of temperature up to 1000 °C, suggesting a continuous conversion before the carbonization completed. It is noteworthy to point out that we did not observe any fragment with the mass greater than 44 in our study.

Because the carbonaceous nitrogen content in the PGM-free catalyst directly correlates to the ORR activity, knowing their formation kinetics is crucial in controlling and optimizing the catalyst synthesis. Nitrogen embedded in carbon is metastable. Retaining a higher level of carbonaceous-N while improving the conductivity through graphitization requires the balance of thermolysis temperature and time. Main decomposition products containing nitrogen include ammonia (mass = 17) and N_2 (mass = 28), both of which were observed in our experiment. Figure 4D shows the NH₃ emission profile with Zn(eIm)₂TPIB having the lowest and Zn(4abIm)₂TPIB the highest onset temperature. The temperature band is relatively broad, from 500 °C to over 900 °C, suggesting a continuous process. The N₂ signal, however, is convoluted by the presence of ethylene, which has the same mass (Figure 4E). To separate ethylene's contribution, we resorted to the signal of ethenyl (mass = 27, Figure 4E inset) as an indicator because they appeared conjointly in the MS spectra. For example, the sharp peak observed for Zn(eIm)₂TPIB at temperature below 600 °C is most likely due to ethylene because it was found in both spectra. Similarly matching peaks observed between 600 °C to 800 °C of all the samples in both spectra can also be attributed to ethylene except for $Zn(Im)_2$ TPIB, of which the peak intensity of mass 28 is significantly higher than that of mass 27 at 800 °C. This further confirms the aforementioned concerted formation of N₂ and C₃H₈ from fragmentation of the imidazolate ring in $Zn(Im)_2TPIB$. The massive N loss gave rise to poor ORR

activity of Zn(Im)₂TPIBP. For the other three PGM-free precursors, TGA shows that N₂ emerged at ca.700 °C and continually increases with temperature after removal of the ethylene background using ethenyl as reference. N₂ evolutions are less facile in Zn(mIm)₂TPIB, Zn(eIm)₂TPIB, and Zn-(4abIm)₂TPIB compared to Zn(Im)₂TPIB, which may be attributed to a competitive path of rearrangement of the imidazole ring with the side chains informing amorphous carbon. For these precursors, however, the nitrogen loss transitioned from ammonia to dinitrogen with the increase of temperature. Investigation of the temperature window for N loss and hydrocarbon fragments revealed the mechanistic insight of the decomposition chemistry of different imidazolates in ZIFs promoted by the presence of iron from TPI. We should point out, however, that we could not identify any fragmented piece from TPI because of its relatively low concentration in the precursors.

In summary, four TPI-added ZIFs containing imidazolate ligands of different side chains (HIm, HmIm, HeIm, and H4abIm) were prepared through a solid-state synthesis, followed by thermolysis to produce Fe/N/C ORR catalysts. The side-chain substitution clearly affects the key structure and composition factors of the final catalyst such as pyridinic-N, SSA, total micropore volume, graphitization level, etc., all of which impact the ORR activity and durability. Additionally, we investigated the imidazolate-to-carbon conversion during the thermolysis and observed a number of temperature-dependent fragmentations associated with the key constituents of the final catalyst, such as nitrogen content. This study provides several findings that can be applied in the rational design, synthesis, and optimization for ZIF-derived materials in energy storage and conversion applications.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergy-lett.9b01740.

Experimental details, electrochemical test results, physical characterization results, structure-property relationship of the studied materials, and ORR activity comparison with the literature (PDF)

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Notes

The authors declare no competing financial interest.

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