IMPERIAL

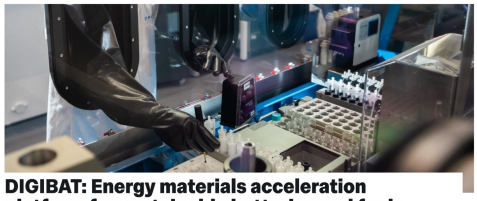
Design of carbon-based electrocatalysts with zeolitic imidazole frameworks

European School of Molecular Nanoscience

Jesús Barrio Hermida, ICRF
Department of Chemical Engineering,
Imperial College London
19/05/2026

1

ICL Department of Chemical Engineering



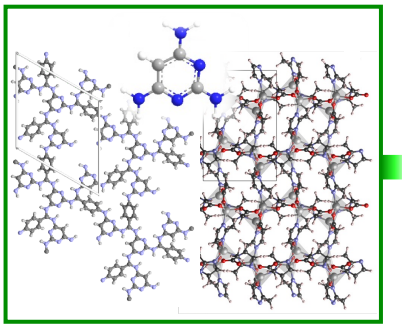
DIGIBAT: Energy materials acceleration platform for sustainable batteries and fuels.

ATLAS AUTOMATED HIGH-THROUGHPUT PLATFORM SUITE

2

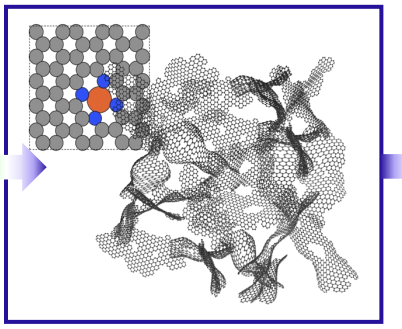
The group

Porous Frameworks



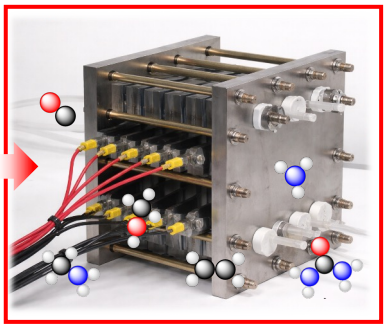
Chem. Eur. J. **2023**
J. Mater. Chem. A **2025**
Adv. Sci. **2025**
Adv. Funct. Mater. **2026**

Carbon-based catalysts



J. Mater. Chem. **2022**
Adv. Mater. **2023**
Green Chem. **2024**
E. Acta. **2024**
Mater. Adv. **2026**

Electrocatalysis



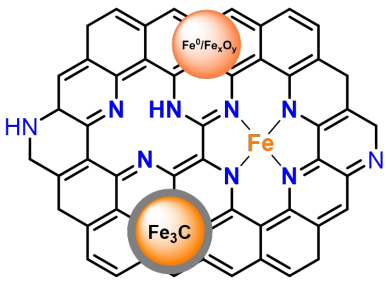
Adv. Funct. Mater. **2023**
E. Acta. **2023**
Commun. Chem. **2025**
Adv. Sci. **2025**

3

Limitation: control over active site density and coordination environment

Fe + N + C

High temperature



- **Electronic conductivity**
- **Accessible surface area**
- **Tunability by insertion of heteroatoms**
- **High atomic utilization**

Conventional synthesis protocols enable poor control over the active site structure

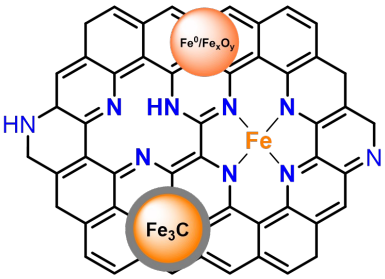
- **Mixture of atomically dispersed sites and metallic aggregates**
- **Inaccessible active sites**
- **Low active site number and utilization**

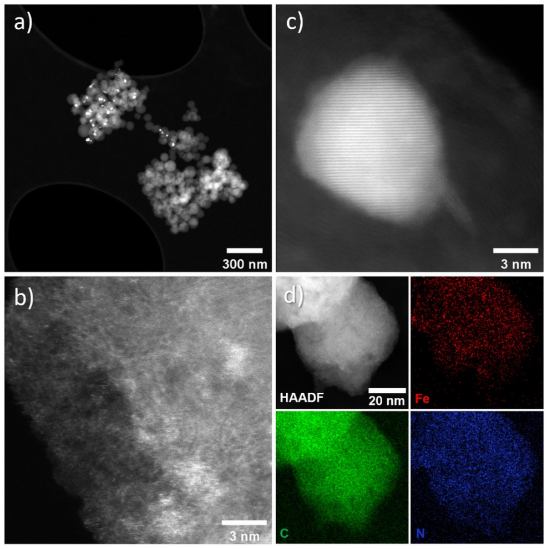
4

Limitation: control over active site density and coordination environment

Fe + N + C

High temperature





Prof. Sarah Haigh

Lorenzo Mazzoli

Mazzoli, Pedersen, Kellner, Hunter, Cai, Wang, Sivula, Haigh, Barrio. *Green Chem.* **2024**

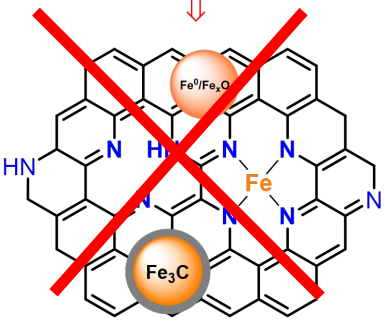
4

5

Limitation: control over active site density and coordination environment

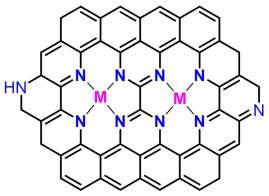
Fe + N + C

High temperature



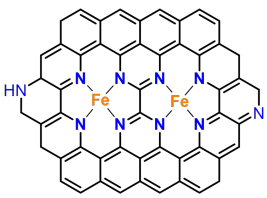
M + N + C

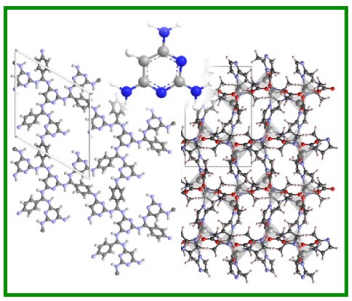
(M = Zn^{2+}, Mg^{2+})



Low temperature

Fe





- **Organic building blocks**
- **Zeolitic Imidazole Frameworks**
- **Hydrogen bonded frameworks**
- **Porous Organic Polymers**
- **Biomass derived chemicals**

Imperial College London

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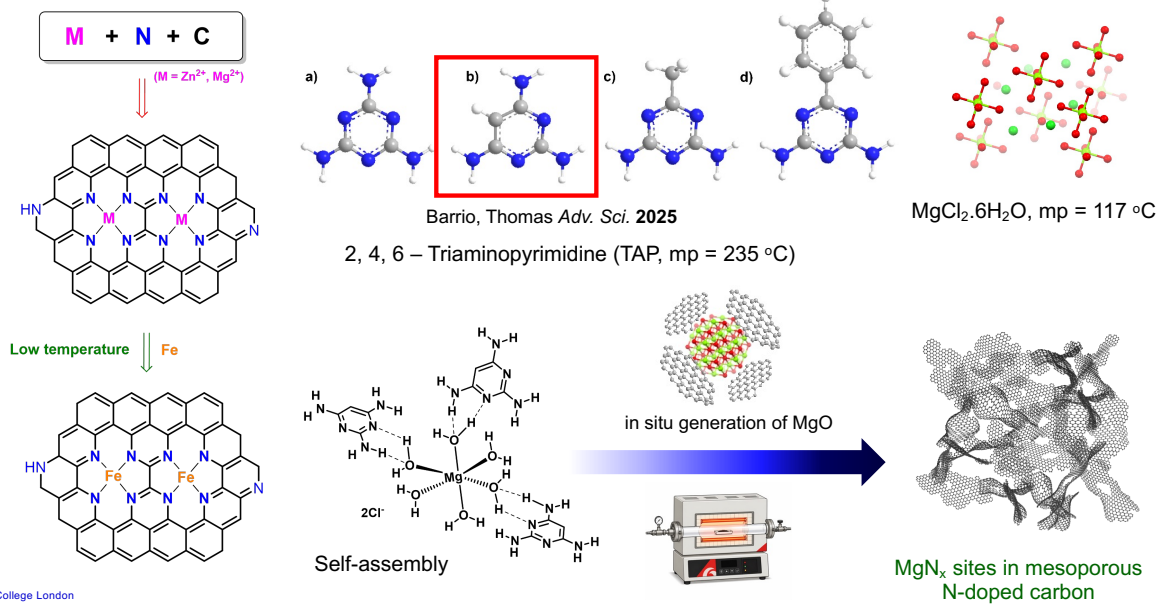
6

A bottom-up approach to engineering active and accessible single sites



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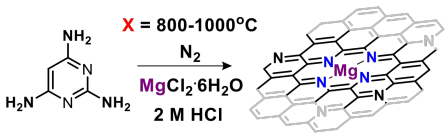
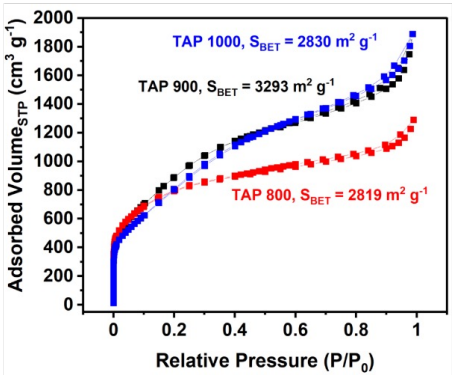
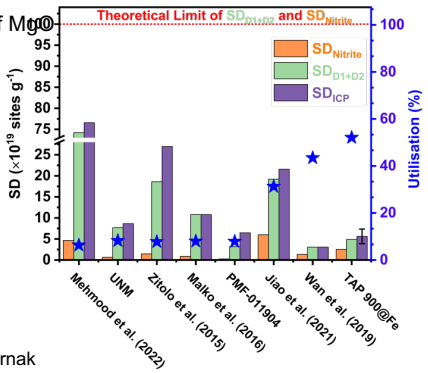
A bottom-up approach to engineering active and accessible single sites



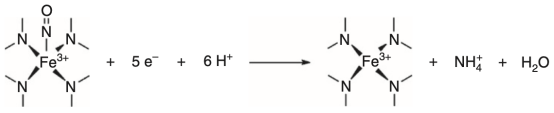
- Active site template
- Porogen via in situ generation of MgO
- >3000 m^2 g^{-1}



> 50% electrochemical utilization



Prof. Anthony Kucernak

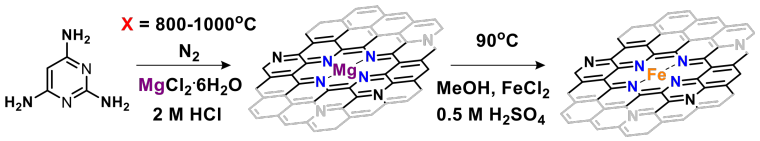


Barrio, Pedersen, Sarma, Bagger, Gong, Favero, Zhao, Garcia-Serres, Li, Zhang, Jaouen, Maillard, Kucernak, Stephens, Titirici. *Adv. Mater.* **2023**

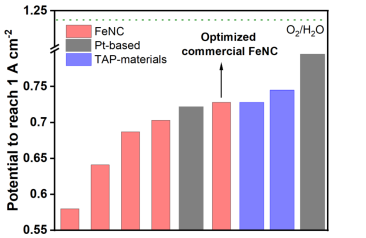
7

8

Electrochemical performance of accessible single sites

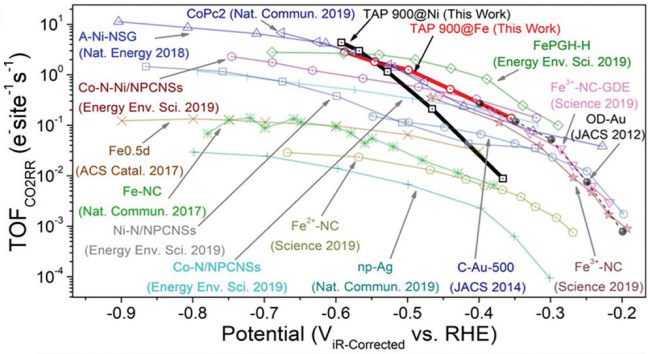


$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$$



Different catalysts tested in alkaline oxygen reduction

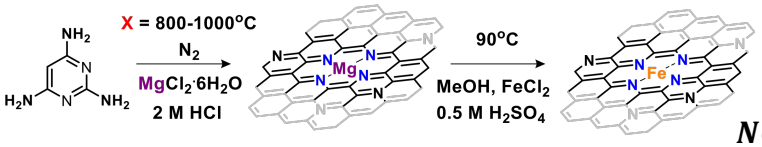
J. Mater. Chem. A **2022**,
J. Power. Sour. **2024**
Energy Environ. Sci. **2024**
Adv. Energy Mater. **2025**
Commun. Chem. **2025**



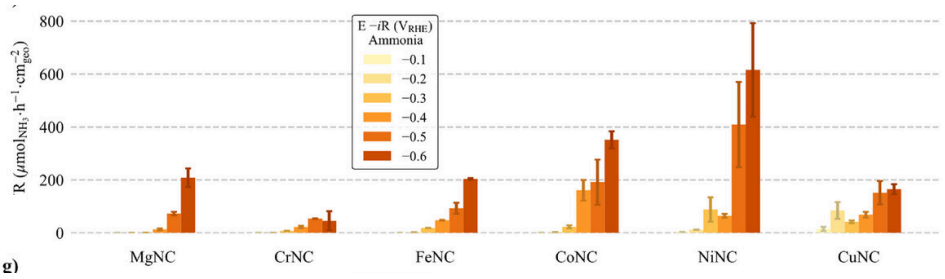
Adv. Funct. Mater. **2023**
E. Acta. **2023**
J. Phys. Mater. **2024**

9

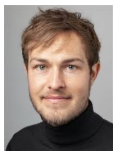
Electrochemical nitrate reduction to ammonia



$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$$
$$NO_3^- + 9H^+ + 8e^- \rightarrow NH_3 + 3H_2O$$



Braga, Pedersen, Riyaz, Barrio, Bagger, Neckel, Mariano, Winkler, Stephens, Titirici, Nagao.
Adv. Sci. **2025**



Prof. Alex Bagger

Prof. Raphael Nagao

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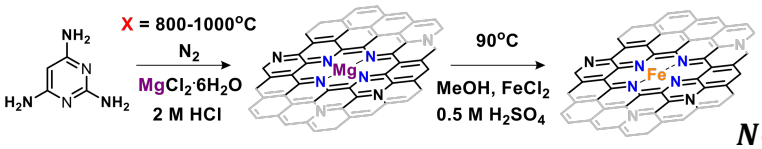
Where now?



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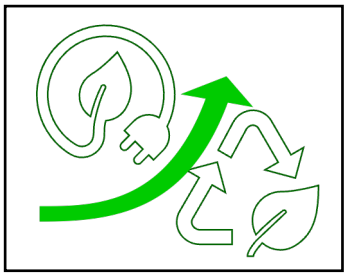
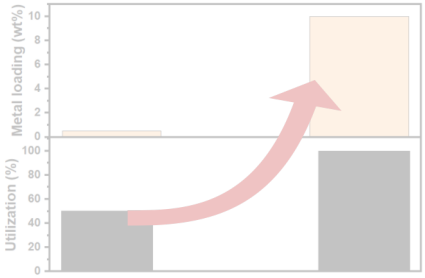
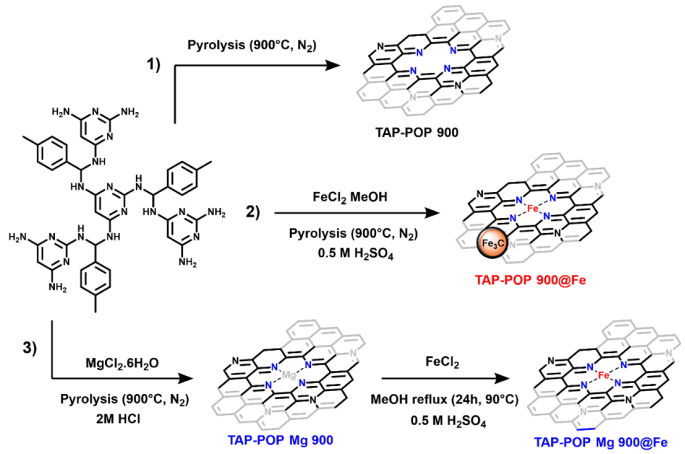
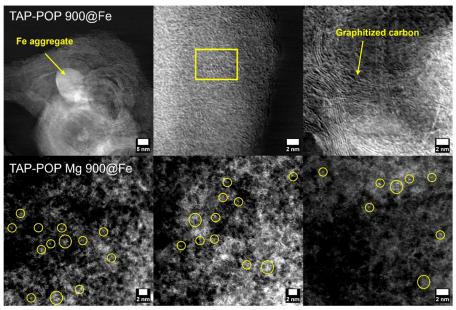


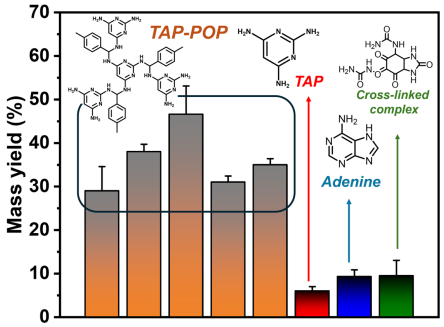


11

Can we make this materials more sustainable?



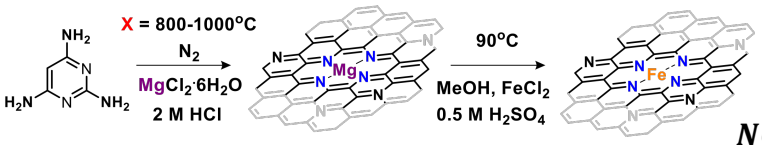




Petitdemange, Zhu, Pedersen, Parker, Balaghi, Li, Favero, Martinez, Haigh, Titirici, Fischer, Barrio. *Adv. Funct. Mater* **2026**.

12

Where now?



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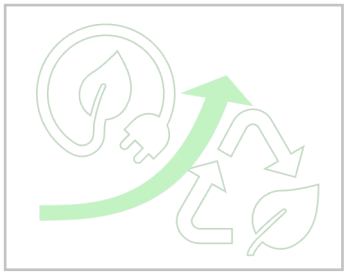
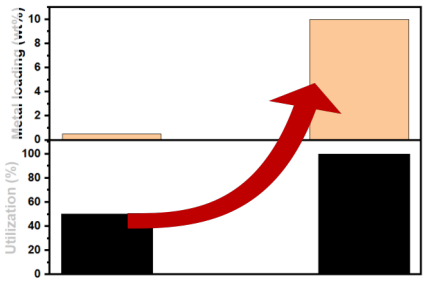
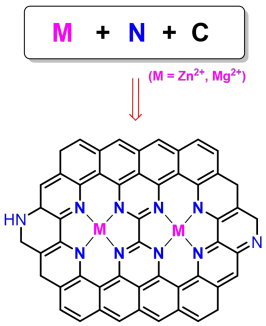


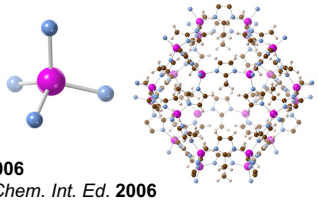


13

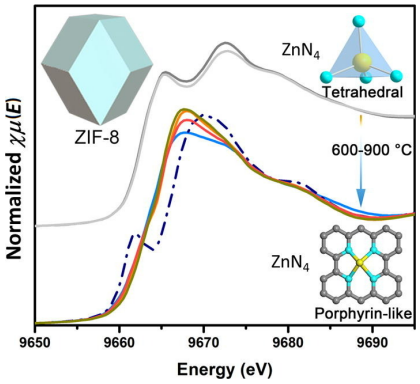
Zeolitic imidazole framework-8 (ZIF-8)



Zn-N_4

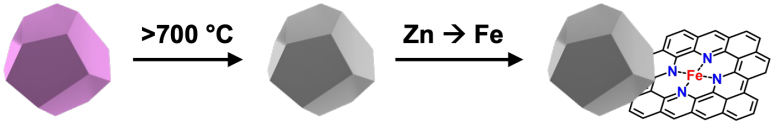


Yaghi. *PNAS* **2006**
Chen. *Angew. Chem. Int. Ed.* **2006**



Waterhouse. *Sci. Bull.* **2020**

ZIF-8 → (>700 °C) → Zn-NC → (Zn → Fe) → Fe-NC

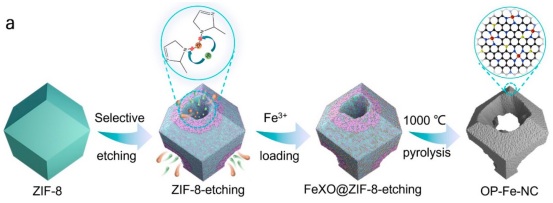


Jiao, …Jaouen, Myers. Nat. Mater. 2021
Mehmood, Gong,…Kucernak. *Nat Catal.* **2022**

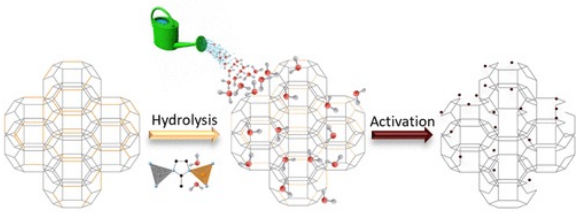
High FeN_x density in microporous N-doped carbon

14

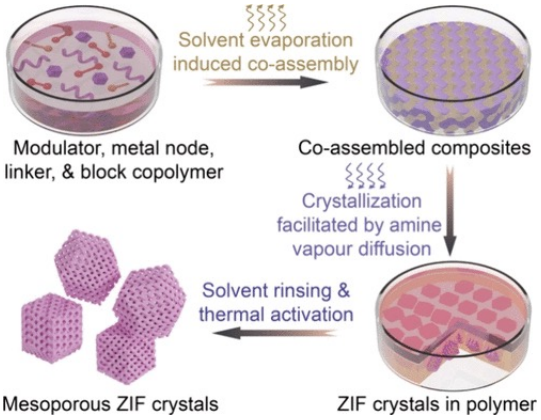
Open porosity in ZIF-8 derived materials



Li, Xia, …, Yamauchi. *J. Am. Chem. Soc.* **2023**



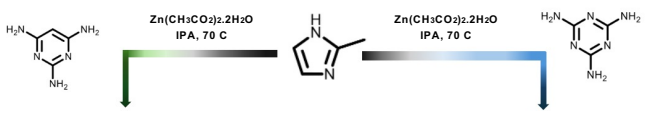
Leon-Alcaide, Lopez-Cabrelles, …, Espallargas. *J. Am. Chem. Soc.* **2023**

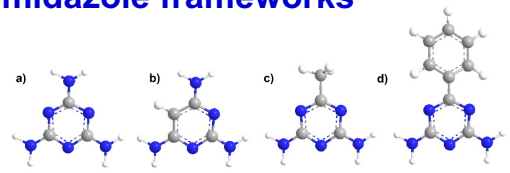


Liu, …, Fairen-Jimenez, Hudson. *J. Am. Chem. Soc.* **2025**

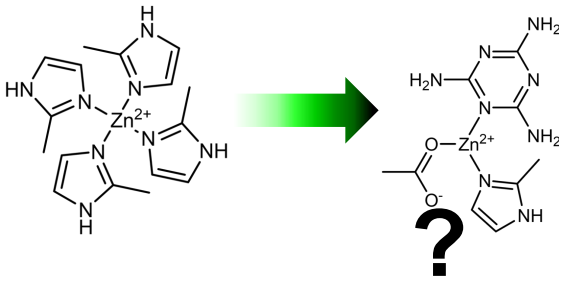
15

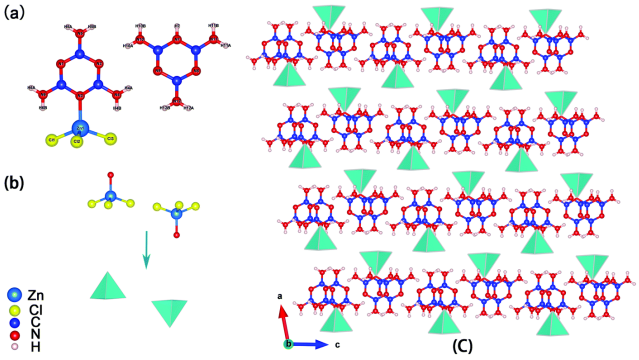
Impact of heterocyclic amines in zeolitic imidazole frameworks





Barrio, Thomas *Adv. Sci.* **2025**

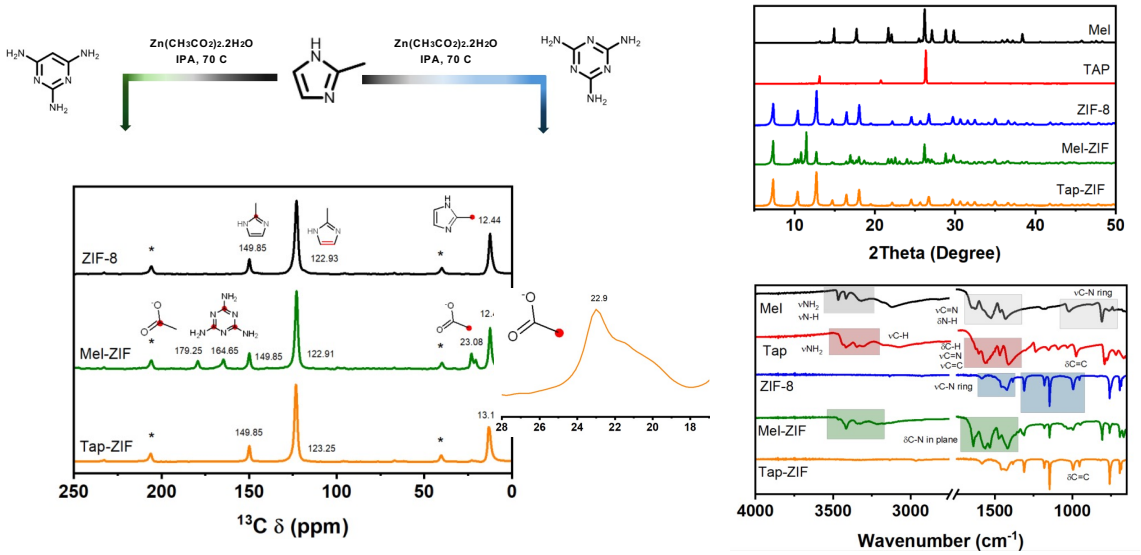




Liu. *J. Mater. Chem. C.* **2021,** 9, 7452-7457

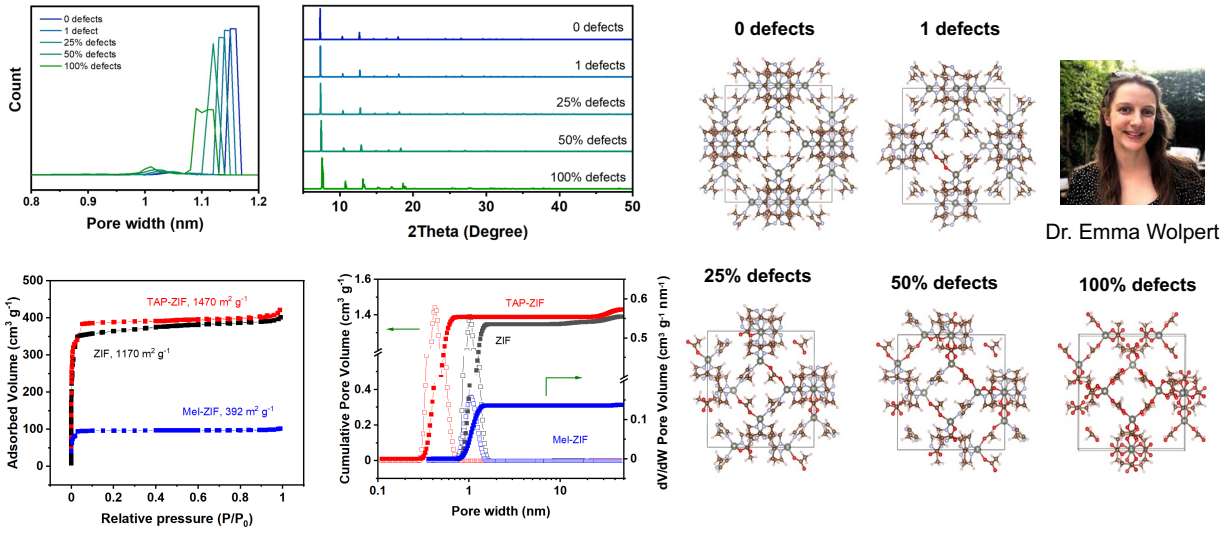
16

Impact of heterocyclic amines in zeolitic imidazole frameworks



Castells-Gil, Zhu, Itskou, Wolpert, Hunter, Tidey, Pedersen, Solvay, Tyrrell, Petit, Barrio. *J. Mater. Chem A.* **2025**

Impact of heterocyclic amines in zeolitic imidazole frameworks



Castells-Gil, Zhu, Itskou, Wolpert, Hunter, Tidey, Pedersen, Solvay, Tyrrell, Petit, Barrio. *J. Mater. Chem A.* **2025**

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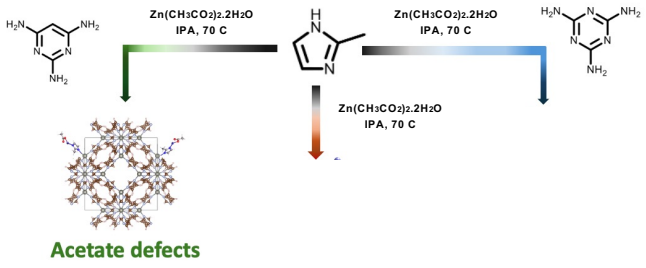
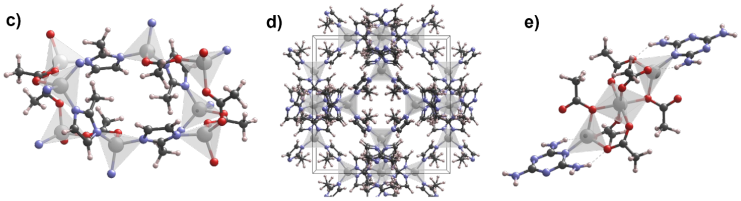
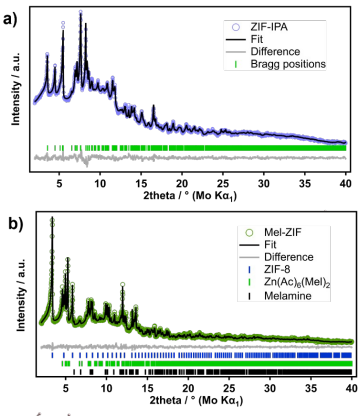


Dr. Jere Tidey

Dr. Javier Castells-Gil

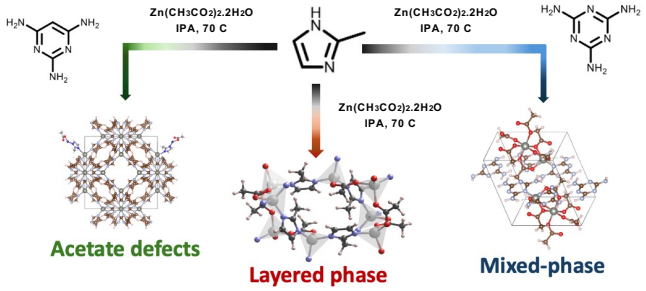


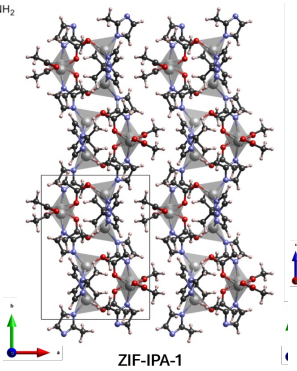
ZIF-IPA | ZIF-8 | $Zn_3(Ac)_6(Mel)_2$

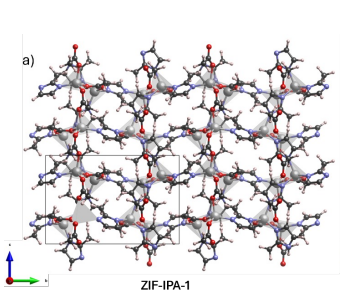


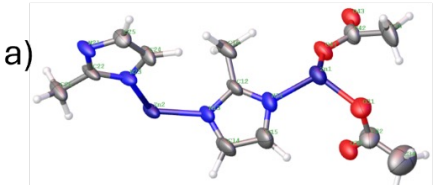
Castells-Gil, Zhu, Itskou, Wolpert, Hunter, Tidey, Pedersen, Solvay, Tyrrell, Petit, Barrio. *J. Mater. Chem A.* **2025**

Impact of heterocyclic amines in zeolitic imidazole frameworks





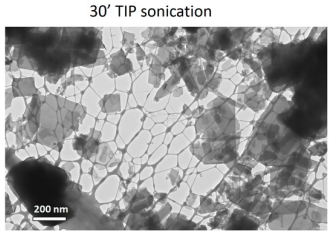


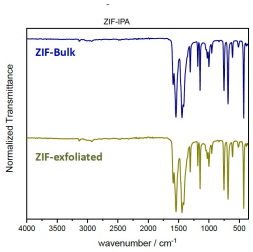


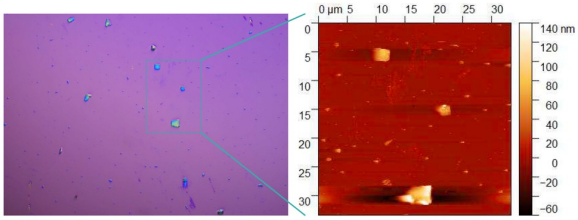
- 2-dimensional ZIF phase
- Interconnected ZnN_3O and $ZnNO_3$ tetrahedra
- Corrugated layers stacked along the *a* axis

Castells-Gil, Zhu, Itskou, Wolpert, Hunter, Tidey, Pedersen, Solvay, Tyrrell, Petit, Barrio. *J. Mater. Chem A.* **2025**

Two-dimensional ZIF

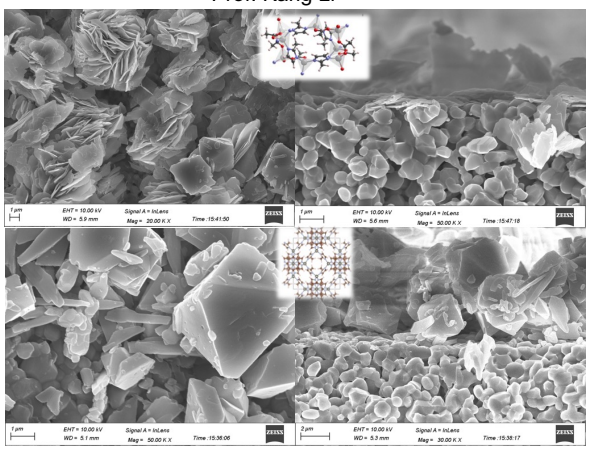




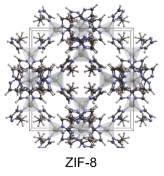


Prof. Kang Li

Dr. Ramon Torres-Cavanillas

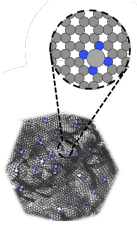


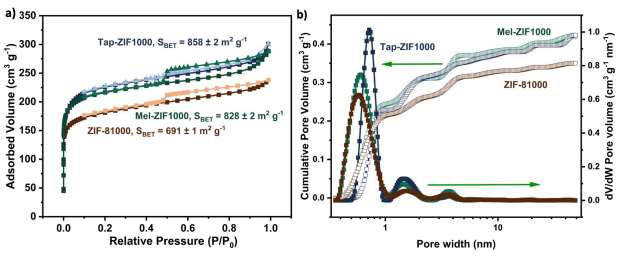
Impact of heterocyclic amines in zeolitic imidazole frameworks

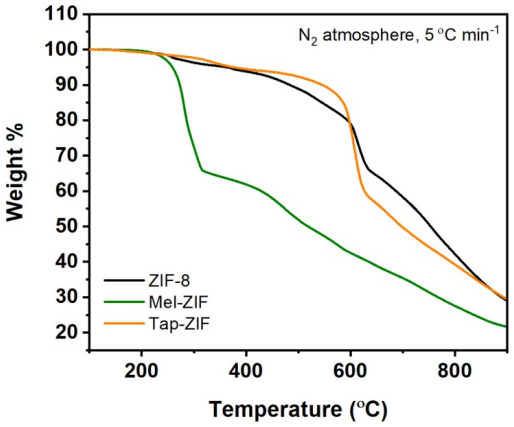


ZIF-8

Thermal conversion







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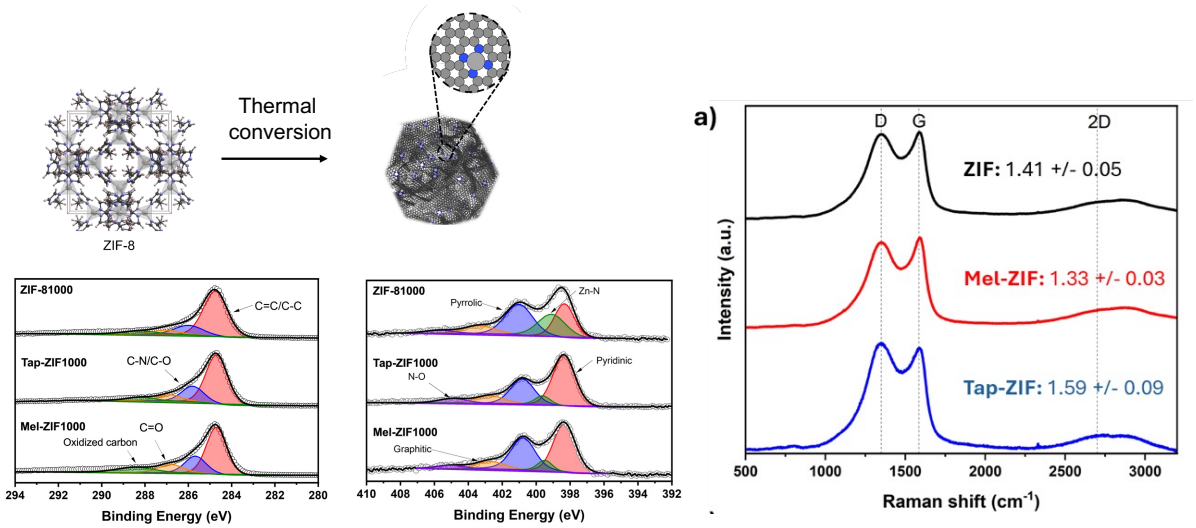

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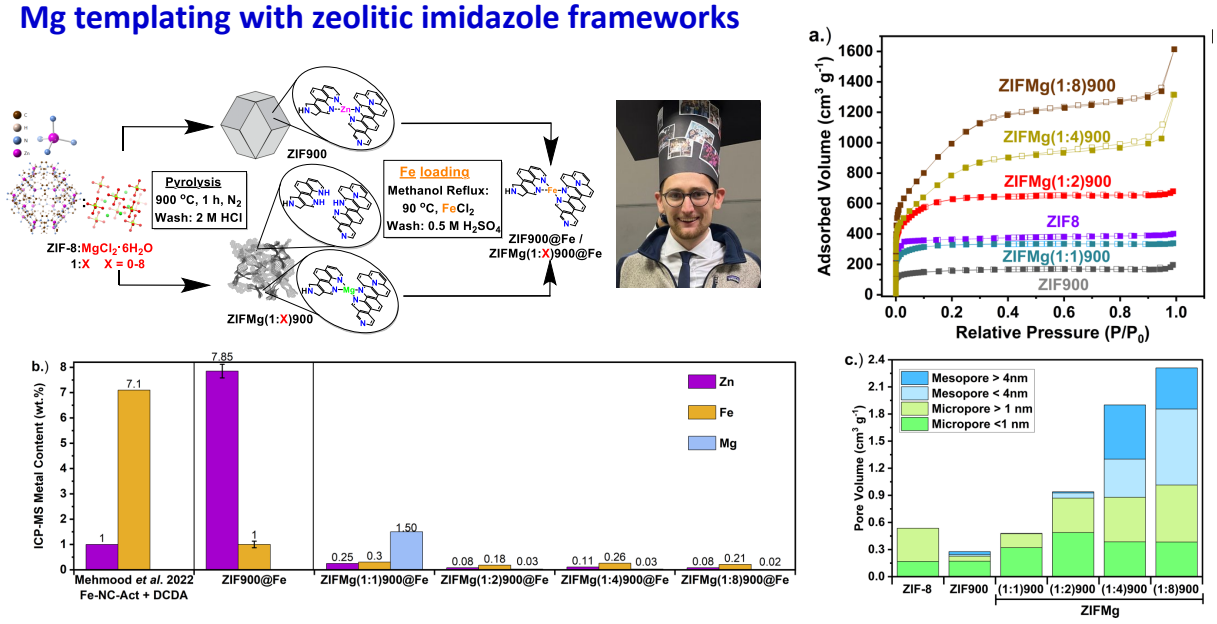
Mg templating with zeolitic imidazole frameworks



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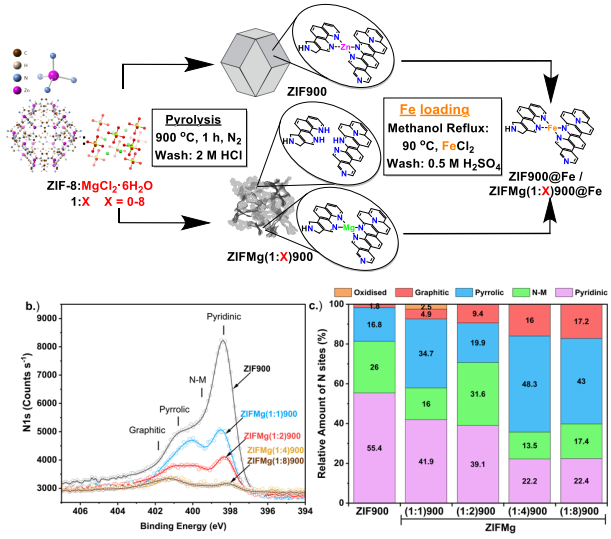
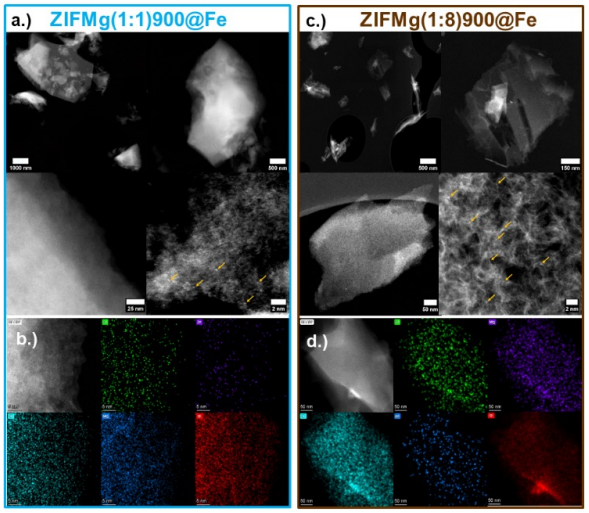
Mg templating with zeolitic imidazole frameworks





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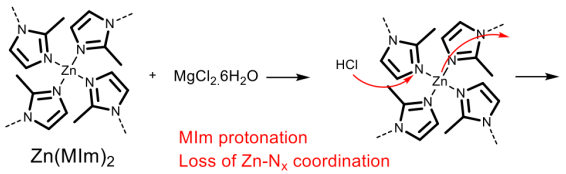
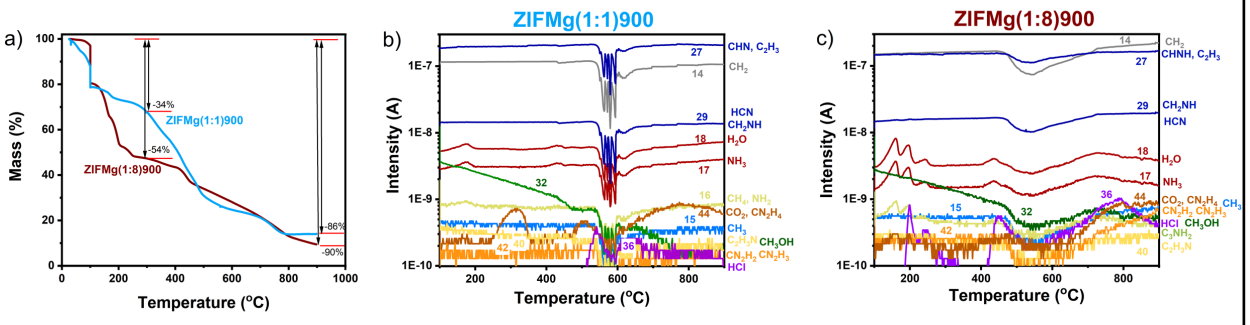
Mg templating with zeolitic imidazole frameworks

$MgCl_2.6H_2O$ degradation
(J. Anal. Appl. Pyrolysis 2011)

$MgCl_2.6H_2O \xrightarrow{\text{dehydration}} MgCl_2.2H_2O \xrightarrow[\text{hydrolysis}]{\text{167 C,}} MgOHCl + HCl + H_2O$





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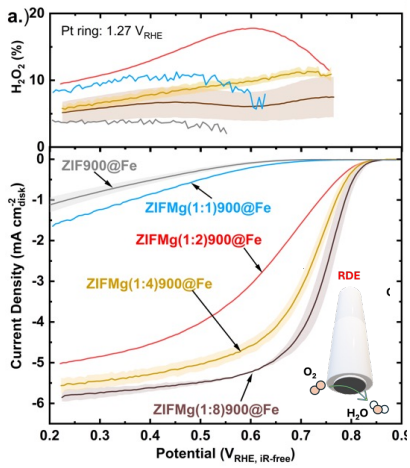
Mg templating with zeolitic imidazole frameworks

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \; E^0 \; [V \; vs \; RHE] = 1.23$$



1-4 nm pore size

ORR activity

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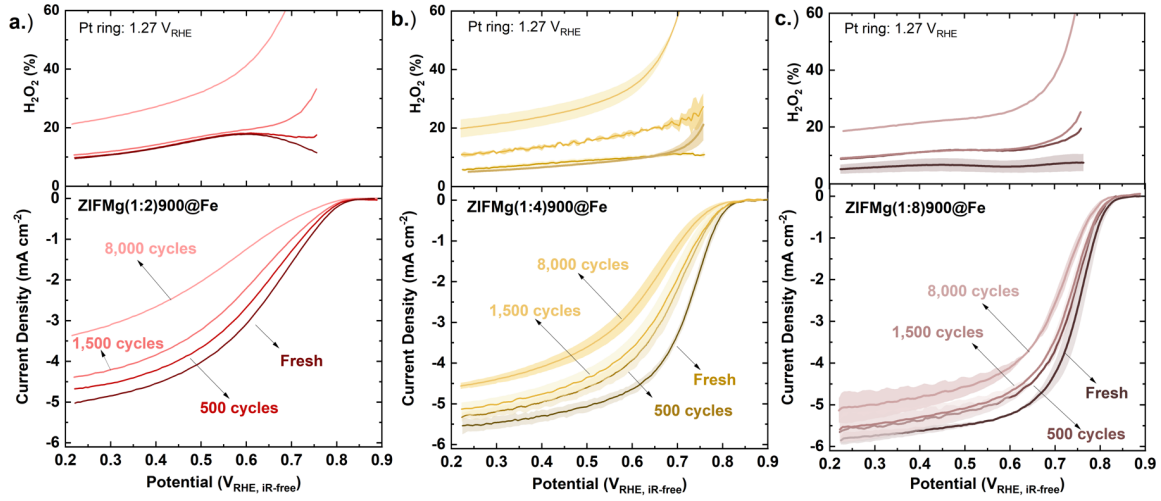
Mg templating with zeolitic imidazole frameworks



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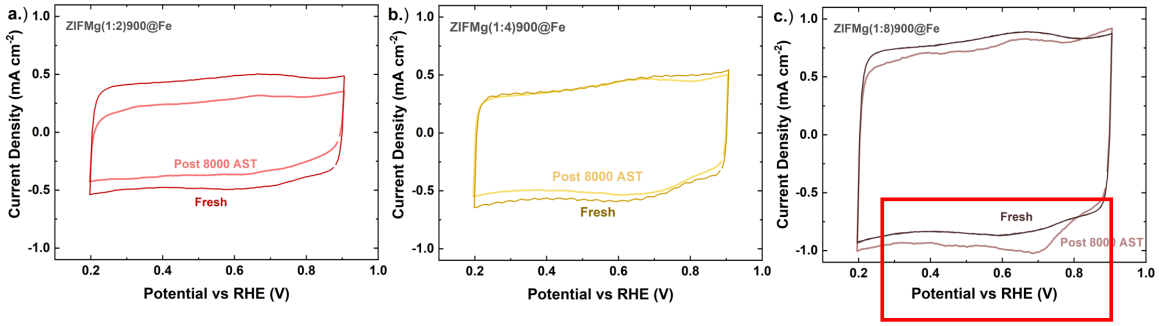
Mg templating with zeolitic imidazole frameworks

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \; E^0\,[V\,vs\,RHE] = 1.23$$

Activity → **Instability**



Defective carbon domains (C-O, C=O…) are preferentially corroded between 0.8 – 0.4 V_{RHE}

Quinone/hydroquinone redox peak

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Take home message

- Heterocyclic amines display differing roles in ZIF-8 synthesis
- Mg^{2+} porogens enable porosity-activity correlations
- More active catalysts display lower stability

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Thank you for your attention

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