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Supporting Information

{Fe^{2+}–Imidazole} Catalyst Grafted on Magnetic {Fe@Graphitized C} Nanoparticles: A Robust Hybrid–Catalyst for H_2 Production from HCOOH

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S1. Sample preparation

Powder X-ray diffraction: Data were acquired over a 2θ range of 10° to 80°. The crystallite size was determined using the Scherrer equation (Eq. S1)[53]

$$d_{\mathrm{XRD}} = \frac{K\lambda}{\mathrm{FWHM} \times \cos\theta} \qquad \text{(Eq.S1)}$$

Where, K = 0.9, λ = 1.5418Å and FWHM is the full width at half-maximum of the XRD peaks. The XRD patterns were acquired in the standard Bragg-Brentano geometry in step scanning mode with a step size of 0.003° and a scan speed of 0.7 seconds per step.

N_2 porosimetry: The SSA equivalent diameter d_{BET} of the particles was calculated by the Eq. S2,

$$d_{\mathrm{BET}} = \frac{6000}{\mathrm{SSA} \times \rho_{\mathrm{Fe@GC}}} \qquad \text{(Eq.S2)}$$

where $\rho_{Fe@GC}$ was calculated based on the percentages of the main crystallographic phases derived from XRD data, i.e. magnetite ($\rho_{Fe_3O_4}$ = 5.17 g/cm^3), wustite (ρ_{FeO} = 5.70 g/cm^3), cementite (ρ_{Fe_3C} = 7.6 g/cm^3), martensite ($\rho_{C_{0.2}Fe_{1.8}}$ = 7.7 g/cm^3) and metallic Fe (ρ_{Fe} = 7.87 g/cm^3).[54–56]

Thermogravimetric analysis (TG-TDA): To assess the efficiency of our catalytic system, the Fe^{2+} loading was estimated based on the incorporation of the organic ligand imidazole. Considering the theoretical stoichiometric ratio of Fe^{2+} to imidazole as 1:2, the organic ligand loading was determined to be 0.36 mmol per gram of Fe@C-graf. Consequently, the corresponding surficial iron loading was calculated to be 0.18 mmol per gram of catalyst.

Transmission Electron Microscopy (TEM): Sample preparation consisted of sonicating powdered samples in ethanol and depositing the homogeneous suspension in the form of a single droplet on a TEM copper grid covered by a lacey carbon film. Before the observations, to remove any organic contamination, samples were treated for 3 s in argon plasma using a Fischione Instruments 1020 Plasma Cleaner.

Table 1 presents phase composition and crystallite size data obtained from X-ray diffraction (XRD) analysis, while specific surface area (SSA) and pore volume were determined via BET analysis. The particle diameter d_{BET} was calculated using Eq. S2.

Supplementary Figure 1

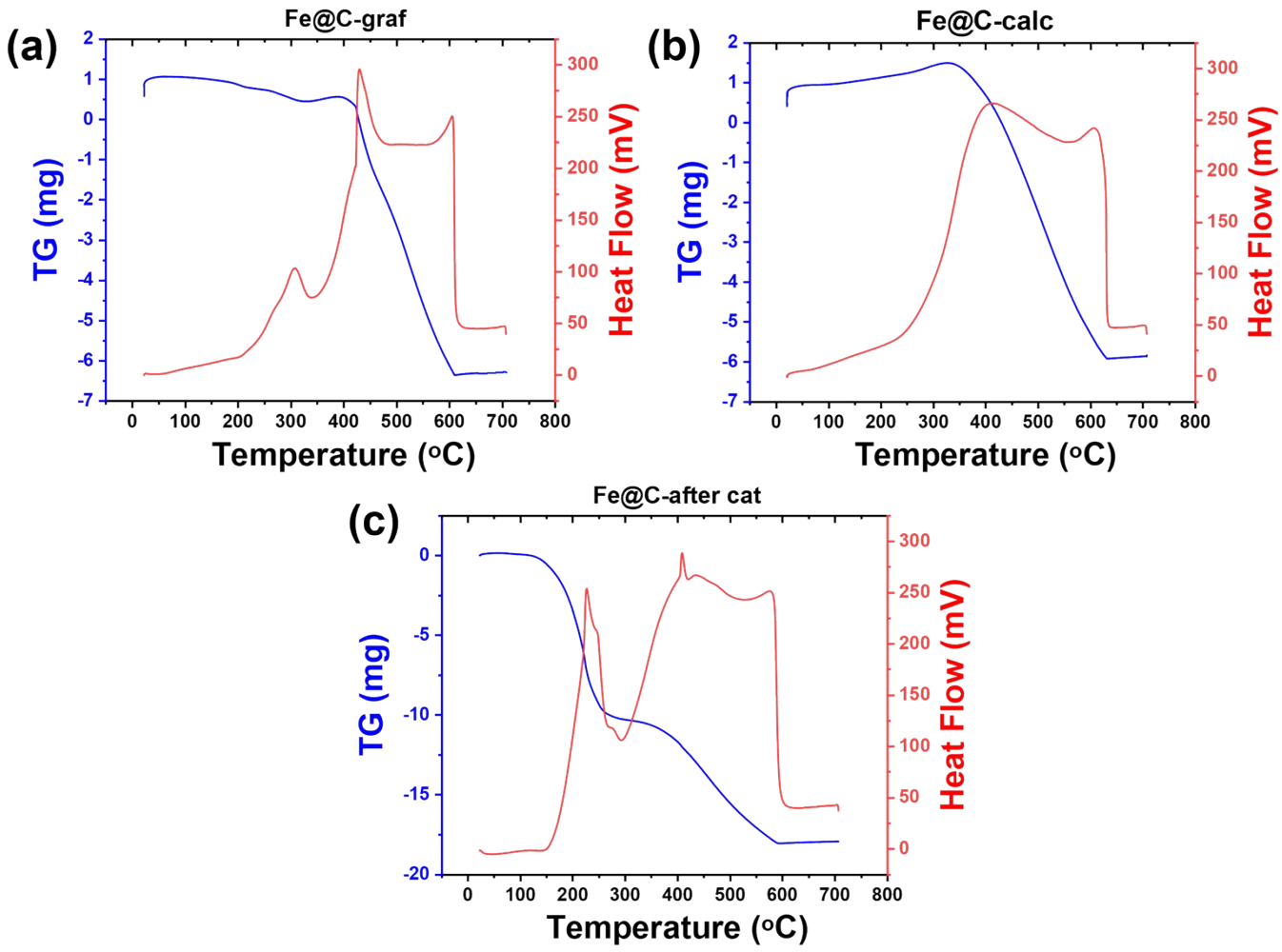
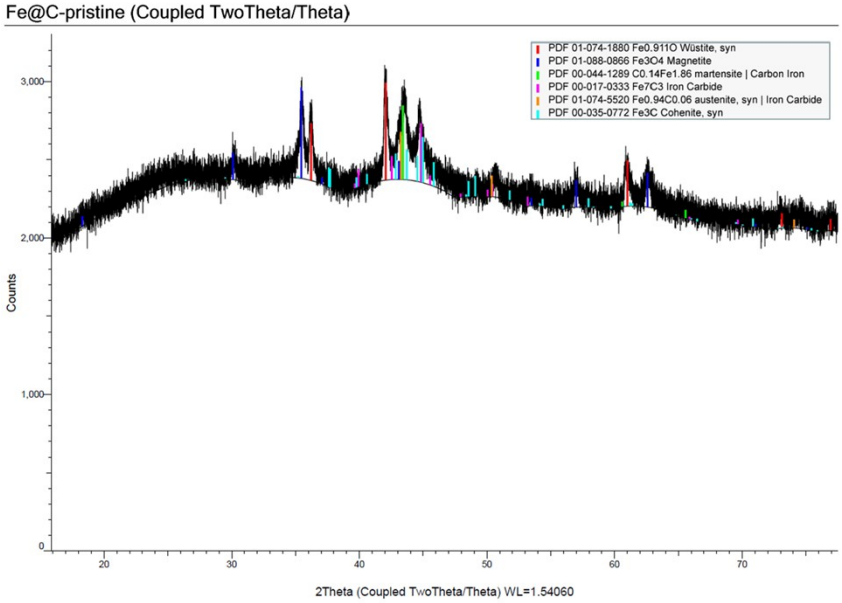


Figure S1. Thermogravimetric analysis of (a) Fe@C@-graf, (b) Fe@C-calc and (c) Fe@C-aftercat.

Supplementary Figure 2

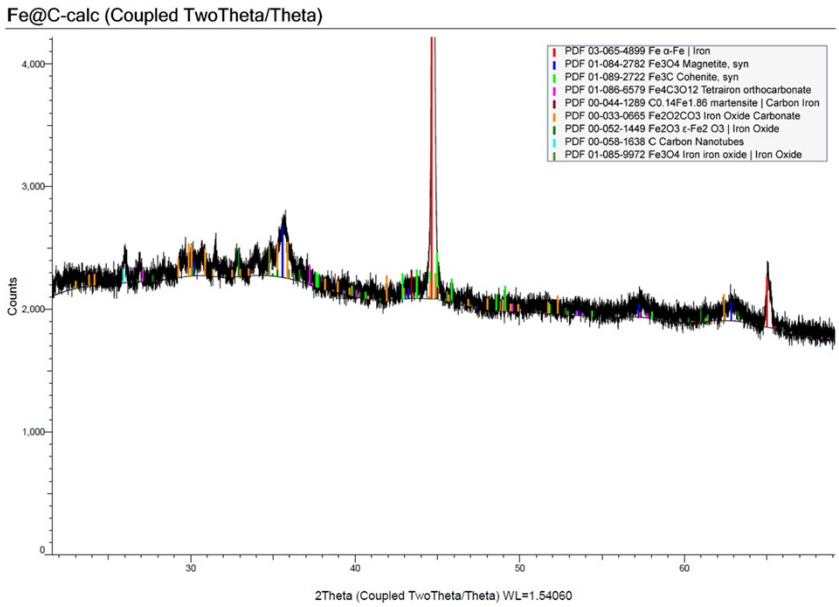
(a)



Crystallographic phases:

- **Wustite FeO**
- **Magnetite Fe_3O_4**
- **Martensite $C_{0.14}Fe_{1.86}$**
- **Iron Carbide Fe_7C_3**
- **Austenite $Fe_{0.94}C_{0.06}$**
- **Cohenite Fe_3C**

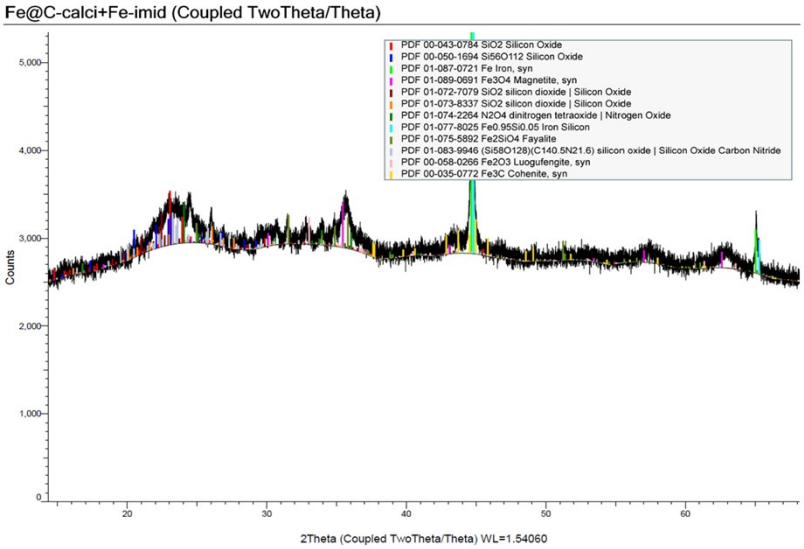
(b)



Crystallographic phases:

- **Iron Fe**
- **Magnetite Fe_3O_4**
- **Martensite $C_{0.14}Fe_{1.86}$**
- **Iron Carbide Fe_7C_3**
- **Tetrairon orthocarbonate $Fe_4C_3O_{12}$**
- **Luogufengite ε-Fe_2O_3**
- **Cohenite Fe_3C**
- **Carbon C**

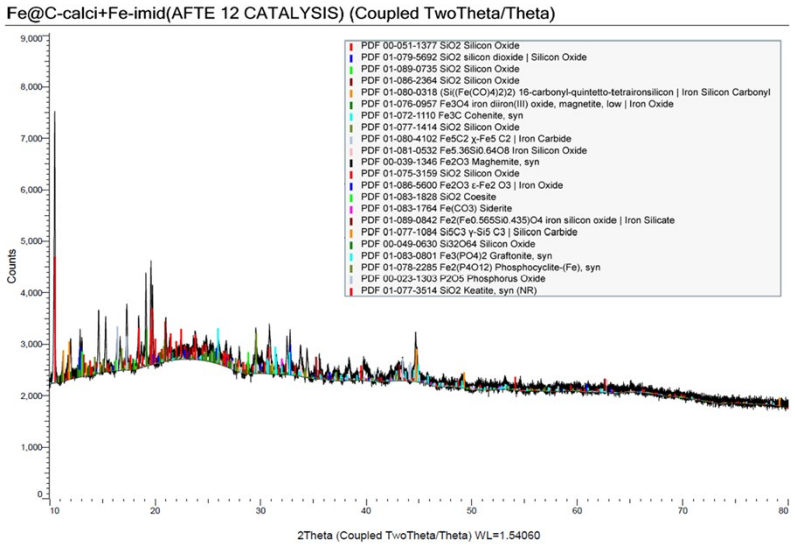
(c)



Crystallographic phases:

- **Silicon Oxide SiO_2**
- **Fayalite $FeSiO_4$**
- **Iron Fe**
- **Silicon Oxide Carbon Nitride**
- **Iron Silicon $Fe_{0.95}Si_{0.05}$**
- **Magnetite Fe_3O_4**
- **Luogufengite ε-Fe_2O_3**
- **Cohenite Fe_3C**
- **Dinitrogen Tetraoxide N_2O_4**

(d)



Crystallographic phases:

- **Silicon Oxide SiO_2**
- **Magnetite Fe_3O_4**
- **Maghemite Fe_2O_3**
- **Iron Silicon Carbonyl $Si((Fe(CO)_4)_2)_2$**
- **Siderite $FeCO_3$**
- **Iron Fe**
- **Iron Silicate $Fe_2(Fe_{0.565}Si_{0.435})O_4$**
- **Silicon Carbide Si_5C_3**
- **Iron Carbide Fe_5C_2**
- **Iron Silicon $Fe_{0.95}Si_{0.05}$**
- **Luogufengite ε-Fe_2O_3**
- **Cohenite Fe_3C**
- **Graftonite $Fe_3(PO_4)_2$**
- **Phosphocyclite $Fe_2P_4O_{12}$**
- **Phosphorus Oxide P_2O_5**

Figure S2. XRD patterns of (a) Fe@C-prist, (b), Fe@C-calc, (c) Fe@C-graf and (d) Fe@C-aftercat (12 uses) analyzed using EVA software, identifying the corresponding XRD crystallographic phases.

Supplementary Figure 3

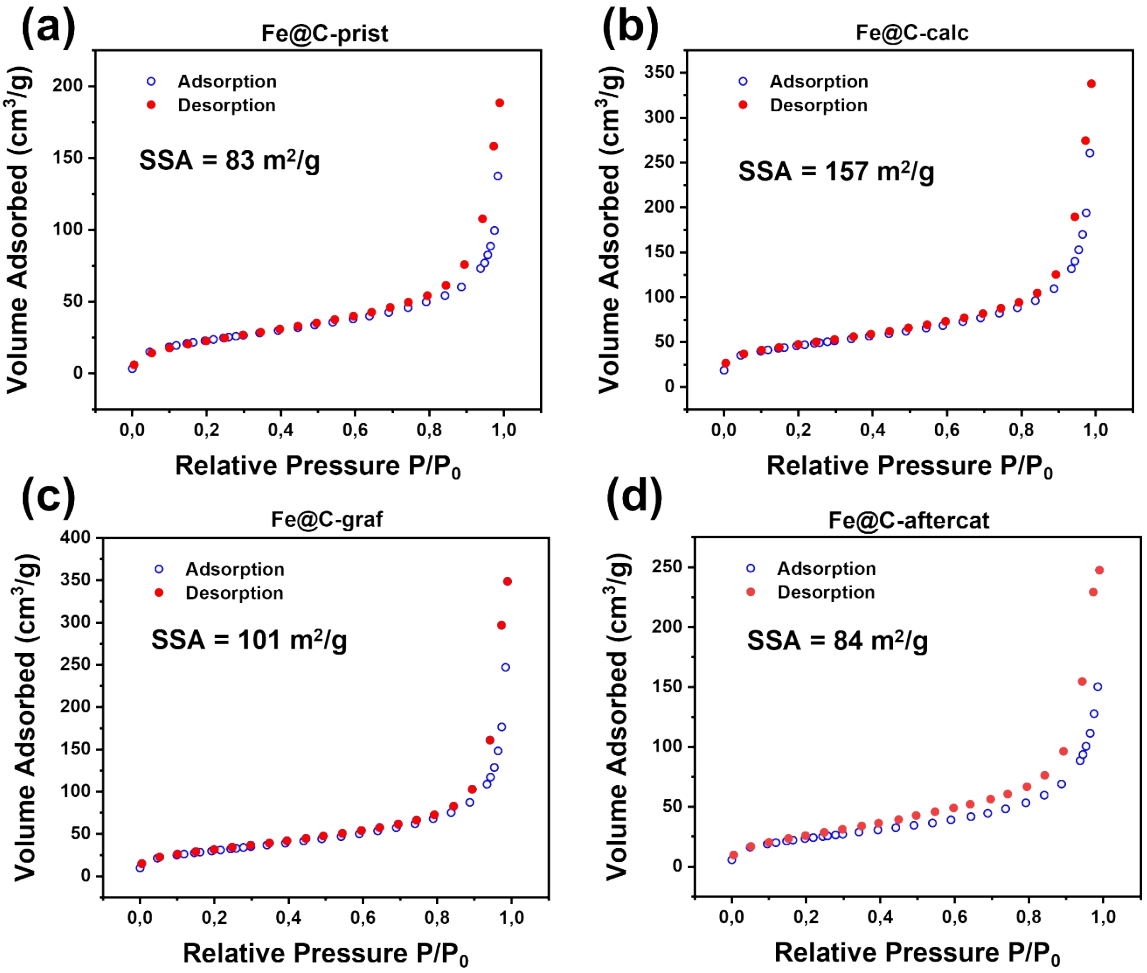


Figure S3. N_2 adsorption-desorption isotherms of hybrid magnetic {Core@Shell Fe@Carbon}@{Fe^{2+}–Imidazole} catalytic materials: (a) Fe@C-prist, (b), Fe@C-calc, (c) Fe@C-graf and (d) Fe@C-aftercat (12 uses).

Supplementary Figure 4

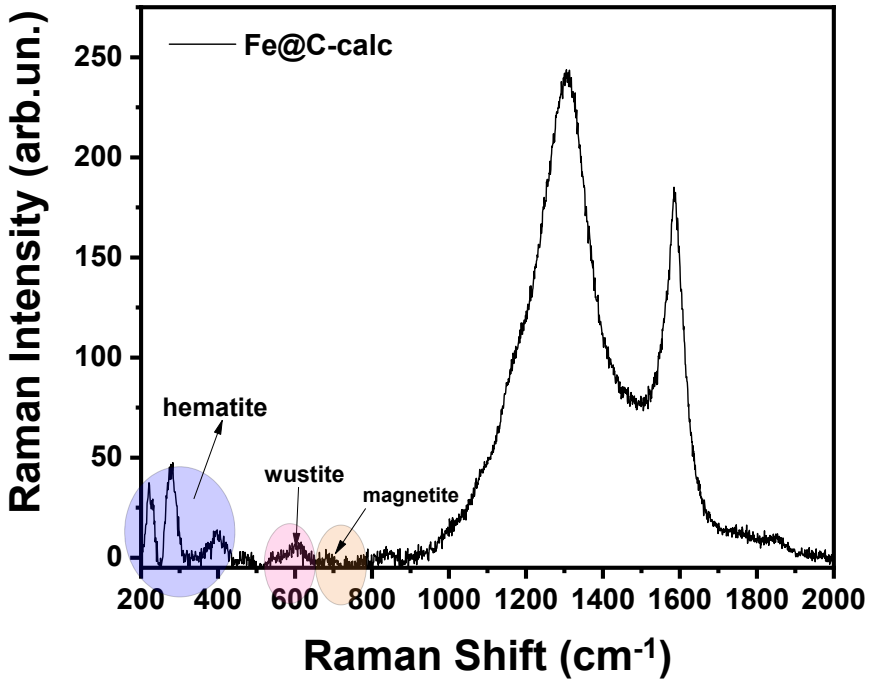
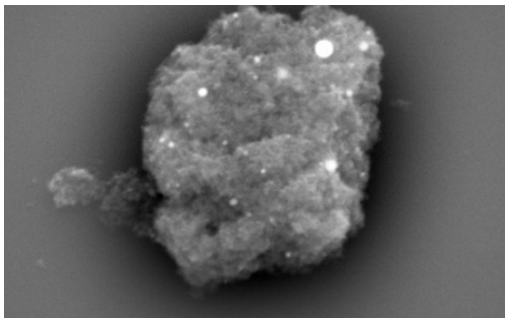


Figure S4. Raman spectrum of Fe@C-calc material showing the oxidation phases of wustite, specifically hematite and magnetite.

Supplementary Figure 5

a) Fe@C-prist

Cut out of map (resolution: 960×600 points)



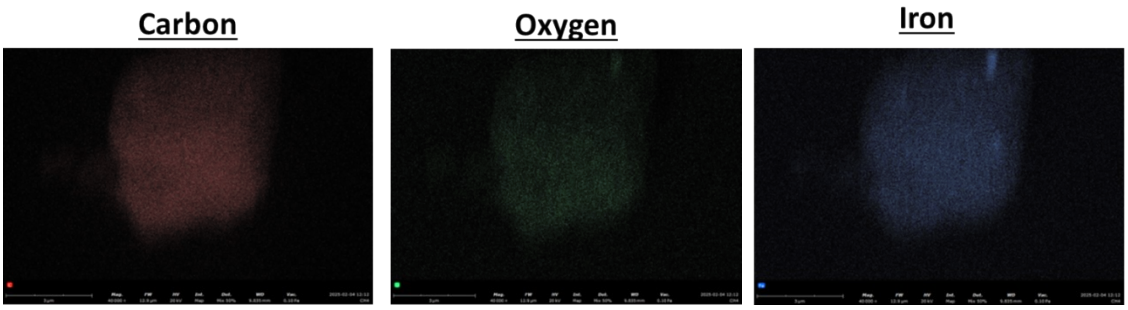
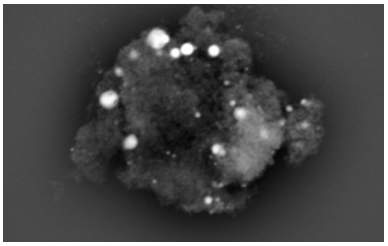


Table S1. EDS analysis for Fe@C-prist.

Element Number	Element Symbol	Element Name	Atomic Conc. (%)	Weight Conc. (%)
6	C	Carbon	61.05	44.80
8	O	Oxygen	31.92	31.20
26	Fe	Iron	7.03	24.00

b) Fe@C-calc

Cut out of map (resolution: 960×600 points)



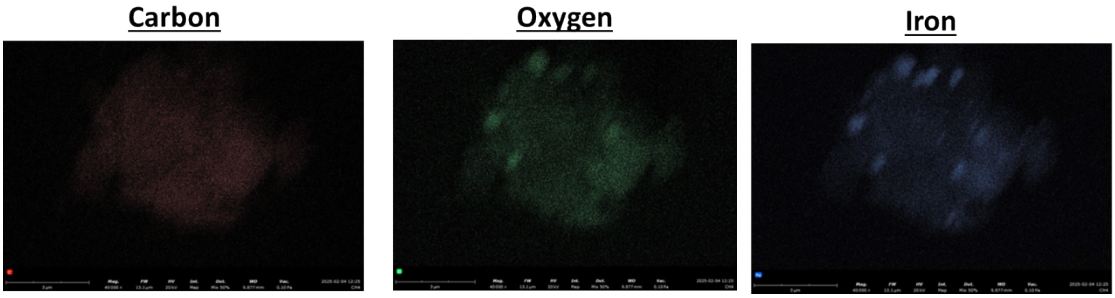
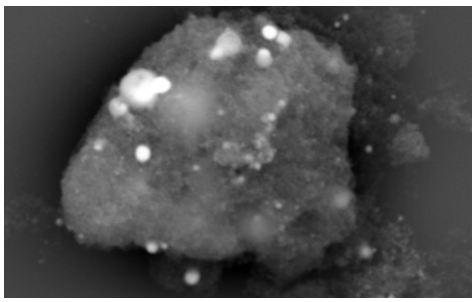


Table S2. EDS analysis for Fe@C-calc.

Element Number	Element Symbol	Element Name	Atomic Conc. (%)	Weight Conc. (%)
6	C	Carbon	47.98	30.20
8	O	Oxygen	39.48	33.10
26	Fe	Iron	12.54	36.70

c) Fe@C-graf ([{Fe²⁺–imidazole}@{Fe@GC}])

Cut out of map (resolution: 960×600 points)



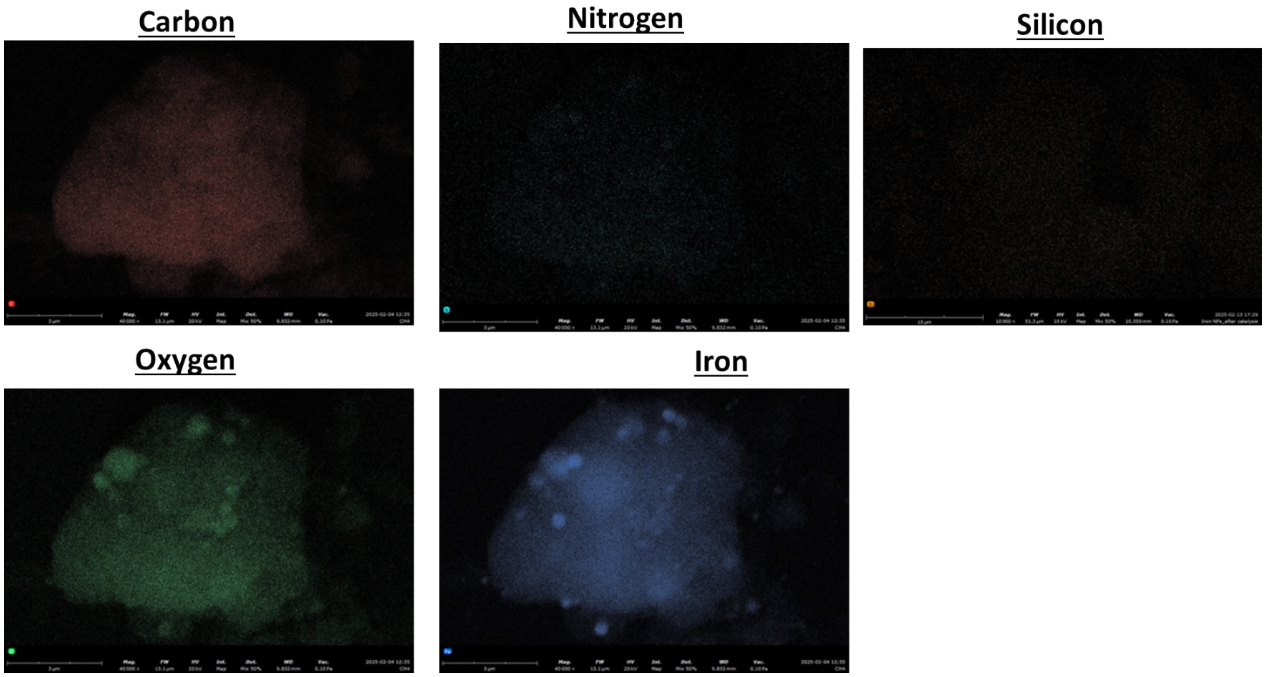


Table S3. EDS analysis for Fe@C-graf ([{Fe²⁺–imidazole}@{Fe@GC}]).

Element Number	Element Symbol	Element Name	Atomic Conc. (%)	Weight Conc. (%)
6	C	Carbon	54.767	37.50
7	N	Nitrogen	2.51	1.50
8	O	Oxygen	31.36	28.50
14	Si	Silicon	1.003	0.90
26	Fe	Iron	10.36	31.60

d) Fe@C-aftercat

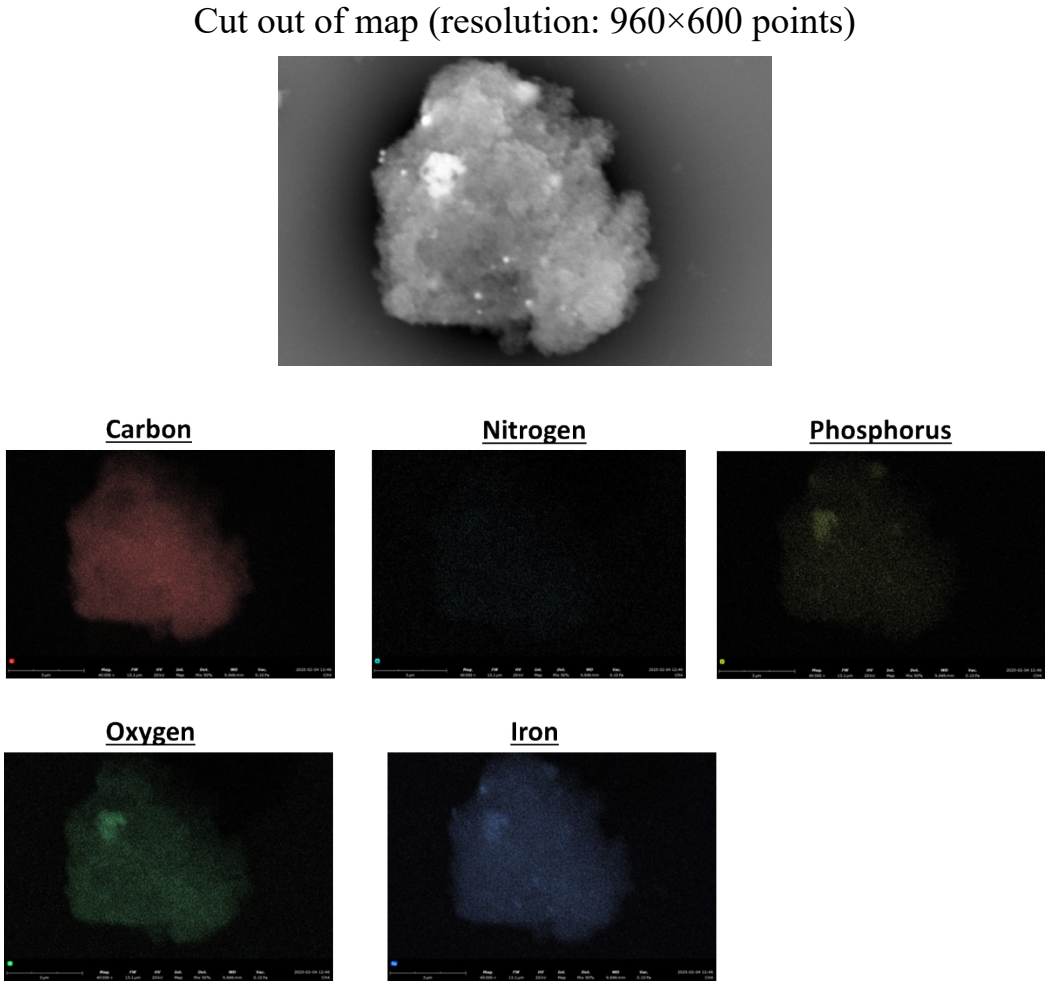


Table S4. EDS analysis for Fe@C-aftercat (12 uses).

Element Number	Element Symbol	Element Name	Atomic Conc. (%)	Weight Conc. (%)
6	C	Carbon	54.284	34.90
7	N	Nitrogen	1.27	1.18
8	O	Oxygen	30.04	27.35
15	P	Phosphorus	2.516	4.61
26	Fe	Iron	11.89	31.96

Figure S5. EDS analysis for hybrid magnetic {Core@Shell Fe@Carbon}@{Fe^{2+}–Imidazole} catalytic materials: (a) Fe@C-prist (Table S1), (b), Fe@C-calc (Table S2), (c) Fe@C-graf (Table S3)and (d) Fe@C-aftercat (12 uses) (Table S4).

Supplementary Figure 6

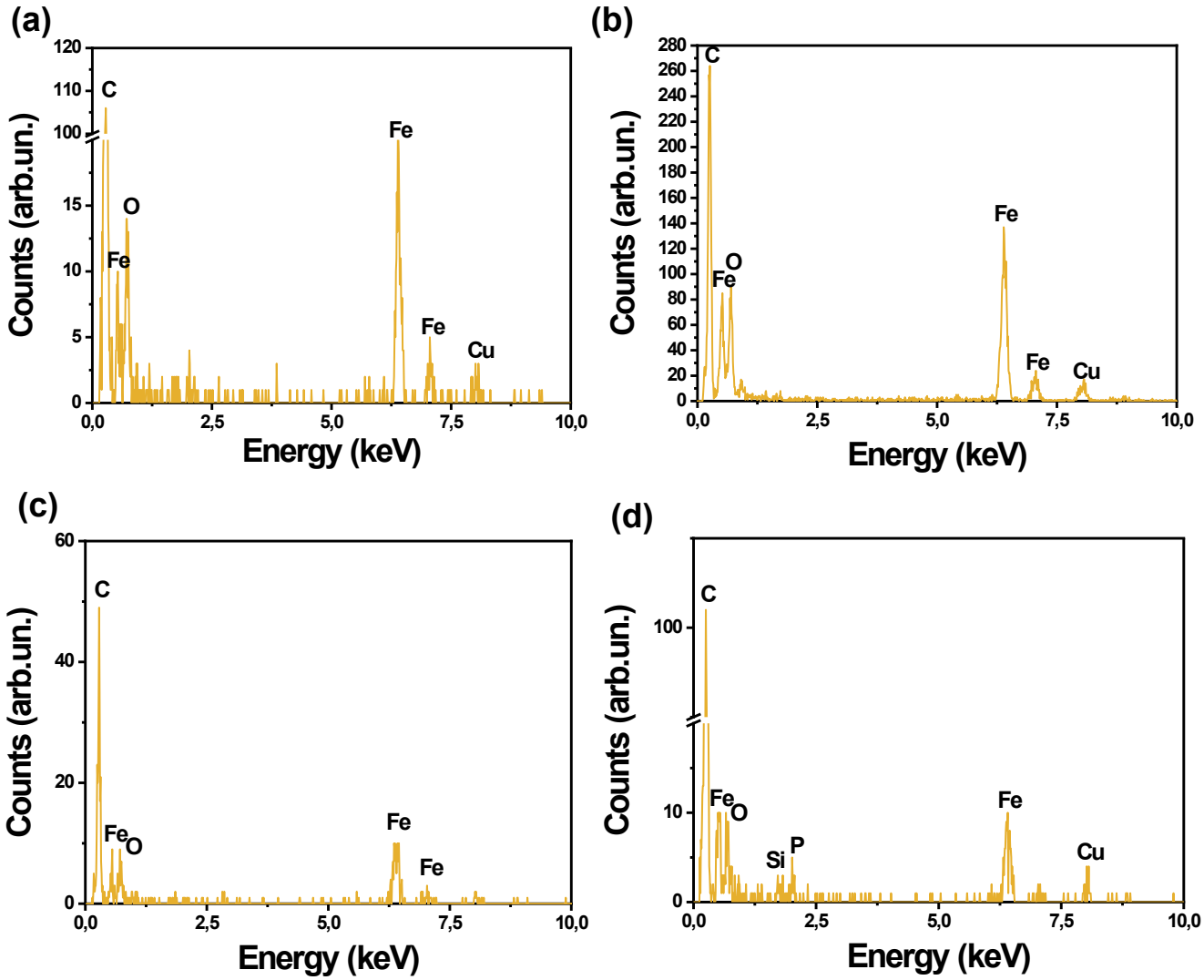


Figure 6. EDS/EDX spectra obtained from TEM/STEM for (a) Fe@C-prist, (b) Fe@C-calc, (c) Fe@C-graf and (d) Fe@C-aftercat (12 uses).

Supplementary Figure 7

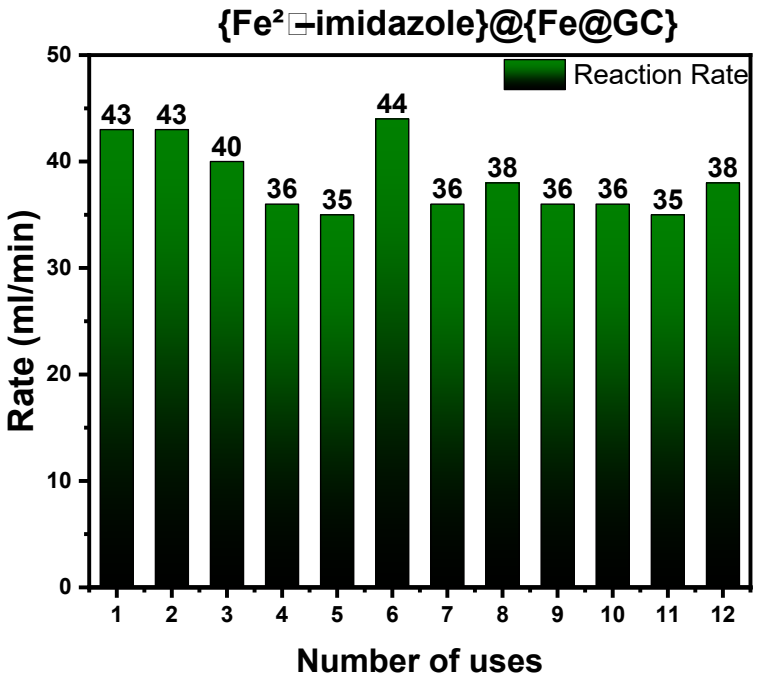


Figure S7. Catalytic reaction rate of {Fe^{2+}–imidazole}@{Fe@GC} for each use.

Supplementary Figure 8

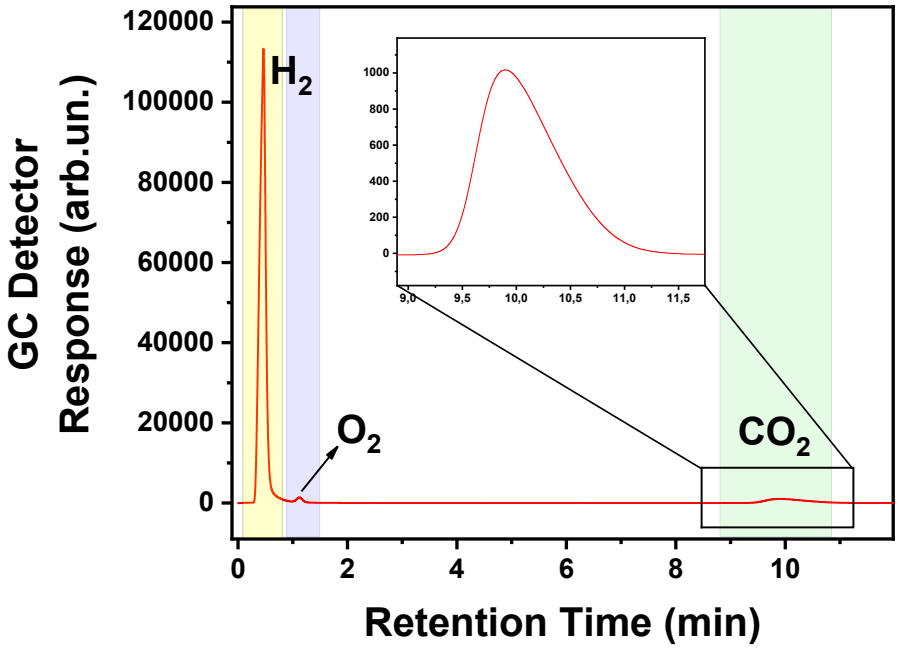


Figure S8. GC spectrum during the catalytic reaction for the [{Fe^{2+}–imidazole/PP_3}@{Fe@GC}] catalytic system.