

Defect engineering-driven tunable porous Fe₃C/Fe@N-CSC via g-C₃N₄ evaporation-etching strategy: dual non-radical pathways of Fe(IV)=O and electron transfer for precision peroxymonosulfate activation



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Introduction

Iron-based catalysts face critical challenges including particle aggregation and limited selectivity in peroxymonosulfate (PMS) activation for contaminant remediation. This study fabricated a hierarchically porous Fe₃C/Fe@N-CSC catalyst via g-C₃N₄-assisted etching. The introduced Fe₃C phase created structural defects, enabling a synergistic "adsorption-catalysis" mechanism. Under optimal conditions (0.2 g/L catalyst, 2 mM PMS), nearly 100% removal of carbamazepine (40 μM) was achieved within 30 minutes. Mechanism investigations confirmed that non-radical pathways, dominated by high-valent iron species (Fe(IV)=O) and electron transfer, were primarily responsible for the degradation. DFT calculations supported the spontaneous chemisorption of PMS on Fe₃C (ΔG = -1.64 eV), which facilitated efficient Fe(IV)=O generation and iron redox cycling. This study develops a Fe-N-C-mediated defect engineering approach to boost PMS activation, providing new insights into non-radical mechanisms of iron-based PMS activation.

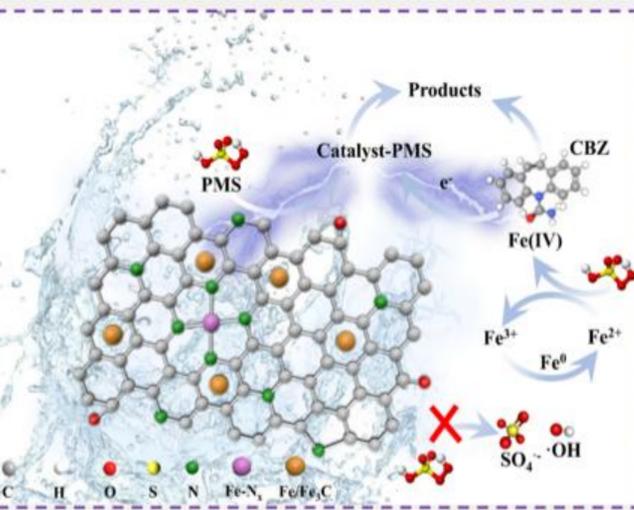


Fig. 1: Mechanism of CBZ Degradation by Fe₃C/Fe@N-CSC Catalyst.

Method

The tunable honeycomb-like layered porous Fe₃C/Fe@N-CSC-a-b was prepared through a simple one-step thermal carbonization method. Here, g-C₃N₄ was introduced not only as a nitrogen source but also as a feasible strategy for regulating the porous structure of the carbon material.

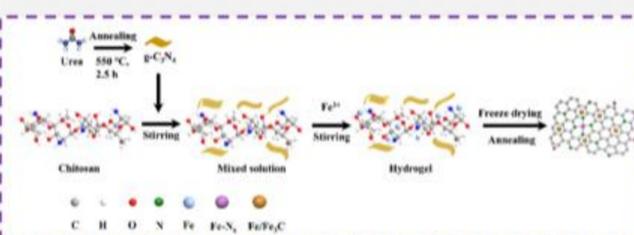


Fig. 2: The synthesis process of Fe₃C/Fe@N-CSC-a-b.

Results

Structural Insights

The Fe₃C/Fe@N-CSC-6-0.5 catalyst was successfully synthesized, exhibiting abundant defects, a high specific surface area, and well-defined active sites.

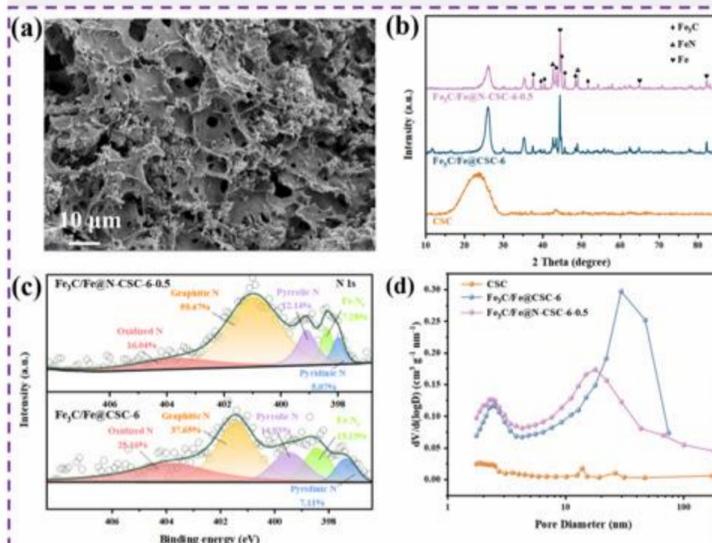


Fig. 3: (a) SEM image, (b) XRD pattern, (c) XPS spectra, and (d) N₂ adsorption-desorption isotherm of Fe₃C/Fe@N-CSC-6-0.5.

Outstanding Catalytic Performance

The catalyst demonstrated broad pH adaptability, stable performance over multiple cycles, and excellent selectivity for electron-rich pollutants.

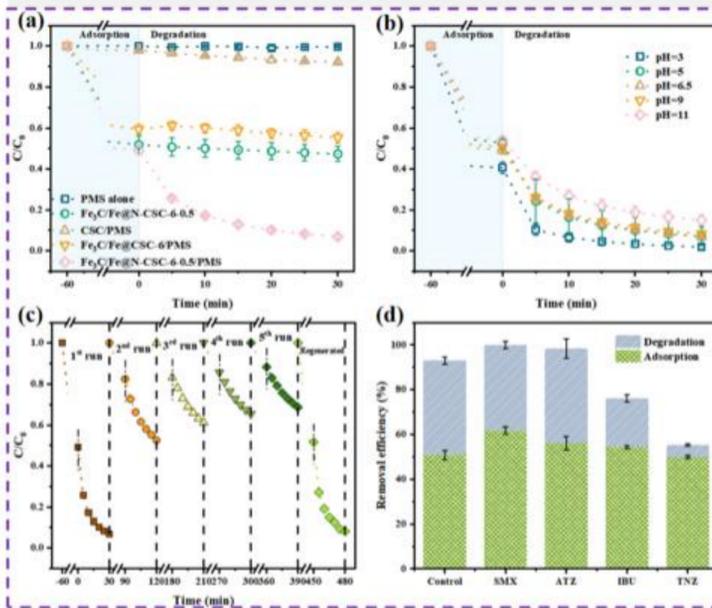


Fig. 4: The effects of (a) different catalytic systems and (b) initial pH value on CBZ degradation efficiency. (c) Recyclability of the Fe₃C/Fe@N-CSC-6-0.5/PMS system. (d) Effects of different organic pollutants on the Fe₃C/Fe@N-CSC-6-0.5/PMS system performance.

Non-Radical Pathways Dominated

Pathway I (Fe(IV)=O): High-valent iron-oxo species are generated through the Fe(II)/Fe(III) redox cycle, which directly attack the pollutant.

Pathway II (Electron Transfer): A catalyst-PMS* complex forms and mediates direct electron extraction from the pollutant.

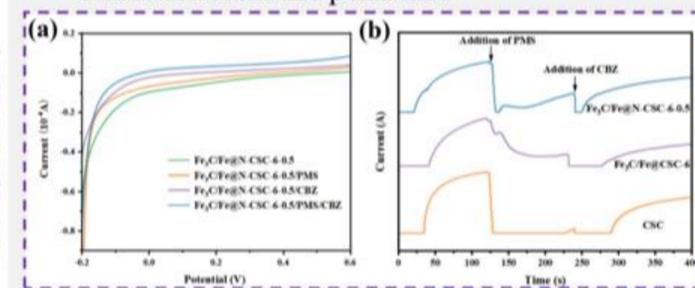


Fig. 5: (a) LSV curves. (b) Chronoamperometric response curves.

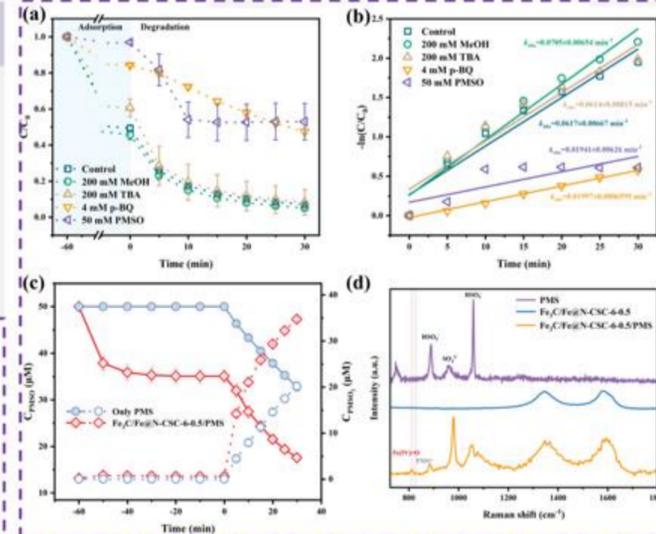


Fig. 6: (a) Effects of different quenchers on CBZ degradation, (b) corresponding pseudo-first-order kinetic fitting. (c) Oxidation of PMSO and generation of PMSO₂. (d) In-situ Raman spectra.

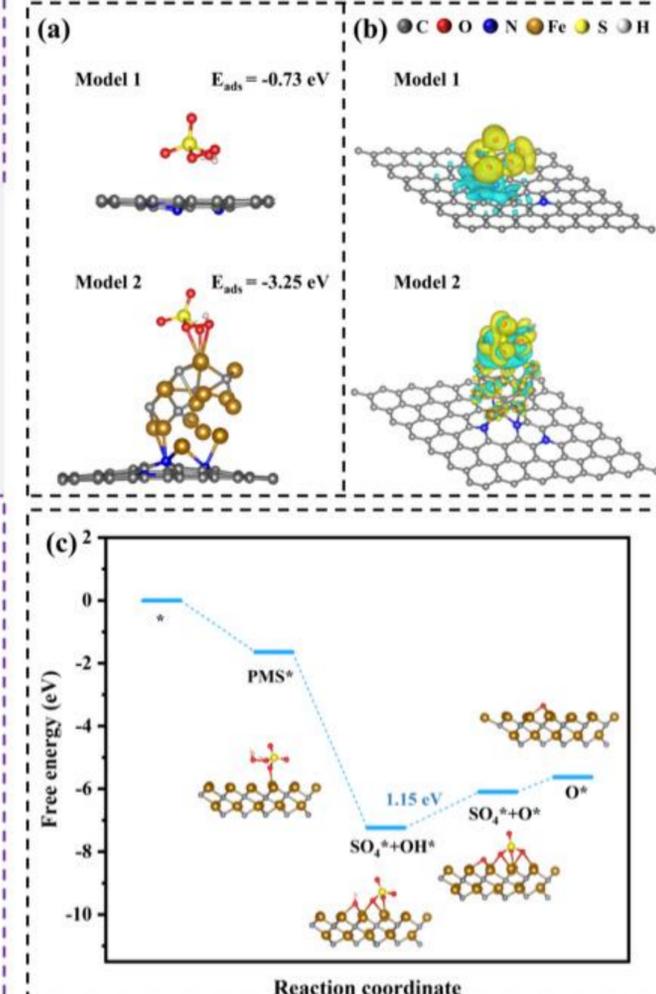


Fig. 7: Adsorption energy (a) and charge density difference distribution (b) of PMS on two models. (c) Free energy diagram.

Discussion

- Developed a g-C₃N₄ evaporation-etching method to synthesize Fe₃C/Fe@N-CSC catalyst.
- Achieved rapid, near-complete CBZ removal via synergistic "adsorption-catalysis".
- Identified a non-radical pathway dominated by Fe(IV)=O and electron transfer.

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