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Advancements in transition metal iron-based catalysts: enhancing catalytic activity through electron transfer

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In this perspective, we aim to explore the latest advancements in a range of design improvements in iron-based catalysts, with a particular focus on electron transfer during catalytic processes. Up to now, various design improvements have been employed to enhance the catalytic activity of heterogeneous iron-based catalysts, including adjustment of microstructure, introduction of support materials, construction of core-shell structures, and incorporation of new components. The effectiveness of these adjustments is contingent upon enhancing the interfacial electron transfer capabilities of heterogeneous iron-based catalysts. Accelerating electron transfer is a fundamental measure to enhance the catalytic ability of the catalyst. Particularly, the activation of pollutants and oxidants during the electron transfer process will lead to different activation mechanisms, combinations, and transformations of activation pathways. Furthermore, considering the practical applications of iron-based composite catalysts, we have also provided future research directions, which address some challenging issues and possible solutions. These directions are crucial for guiding future efforts in catalyst development and optimization.

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1. Introduction

Recent studies have shown that various emerging organic pollutants in the environment, including endocrine disruptors, perfluorinated compounds, antibiotics, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls, are closely linked to human activities. However, traditional treatment techniques fail to effectively break down these contaminants, resulting in significant residues in the environment.¹ Due to their bioactivity and persistence, these pollutants pose potential risks to aquatic ecosystems. Many approaches, such as adsorption, membrane separation, microbial degradation, coagulation, and electrochemical techniques, have been explored by researchers in an attempt to remove wastewater contaminants. Nevertheless, the purifying effectiveness of these approaches still falls short of expectations.² Among many other techniques, sulfate radical-based advanced oxidation processes (SR-AOPs) have shown to be a stable and effective method for the deep treatment of organic pollutants, activating persulfate to generate strong

oxidative reactive oxygen species (ROS) that efficiently degrade organic pollutants.³ Compared to conventional AOPs, SR-AOPs have a greater oxidation potential (2.5–3.1 V), a longer half-life (30–40 μ s), and a wider pH range (2–8); these benefits allow for improved mass transfer and increased effective engagement with target molecules.⁴ Common oxidants in SR-AOPs include peroxydisulfate (PDS, $S_2O_8^{2-}$) and peroxymonosulfate (PMS, HSO_5^-).⁵ Various strategies have been proposed to enhance persulfate activation into ROS for organic pollutant degradation. It is more economical to use abundant transition metals as catalysts rather than energy- or precious metal-based processes.

Transition metals, with their d-orbital electrons or empty d-orbitals, excel at giving or receiving electrons during chemical reactions whose corresponding electron transfer happens to be key to heterogeneous advanced oxidation systems. Iron, manganese, copper, cobalt, and certain compounds comprising one or more of these transition metals are often used as catalysts.⁶ Although strong catalytic activity for the degradation of organic contaminants in SR-AOPs has been documented for copper-based and cobalt-based catalysts, their practical uses are limited due to the environmental hazards posed by the toxic metal ions they emit during the reaction. As a kind of transition metal, iron has the advantages of environmental friendliness, safety and being non-toxic, inexpensive and readily available, as well as having obvious application benefits. Accordingly, iron-based materials are one of the most active frontier

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fields in heterogeneous transition metal catalysis research.⁷ However, the traditional iron-based catalysts are mainly developed and improved around zero-valent iron and oxides, and the high surface energy of their nanostructure is prone to agglomerate in an aqueous solution, resulting in low catalytic activity.^{8–10} Therefore, developing highly active iron-based catalysts and enhancing electron transfer efficiency in catalytic SR-AOPs are absolutely essential to significantly improve catalytic activity. Researchers have implemented a series of design improvements, including adjustment of microstructure, introduction of support materials, construction of core–shell structures, and incorporation of new components.¹¹ In this perspective, the effects of various design improvements on the degradation kinetics of organic contaminants and their impact on the electron transfer mechanism during the catalytic reaction are discussed. Additionally, we propose recommendations for the future research direction of iron-based composite catalysts, involving some drawbacks and challenges to be faced and overcome, as well as possible solutions.

2. Various catalyst design improvements

2.1 Adjustment of microstructure

In terms of catalyst microstructure, many researchers are mainly concerned about the morphological structure of catalysts that are associated with the distribution and coordination of surface active sites. As a result, controlling the morphology of catalysts has become a powerful strategy for enhancing catalytic activity. Chen *et al.* successfully synthesized the oxygen vacancy-enriched ultrathin two-dimensional (2D) Fe₃O₄ nanosheets under dry-chemical conditions, which have a unique graphene-like morphology and enriched oxygen vacancies, and the maximum catalytic activity for the degradation of bisphenol A (BPA) reached 93.2% within 10 min.¹² In addition to initiating the redox cycle of Fe₃O₄, the oxygen vacancy-rich ultrathin 2D Fe₃O₄ significantly reduced the energy barrier for interfacial charge transfer and facilitated the electron transfer between pollutants and persulfate. To investigate the fundamental electron transfer mechanisms, characterization techniques were employed including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).^{13,14} Notably, EIS analysis showed a smaller arc radius in the Nyquist plot for the 2D Fe₃O₄ nanosheets, demonstrating significantly reduced charge transfer resistance along with enhanced electron conduction efficiency compared to conventional catalysts. Complementary CV measurements coupled with density functional theory (DFT) calculations further revealed that surface oxygen vacancies function as electron reservoirs, supplying abundant electrons to BPA molecules—a crucial mechanism enabling efficient interfacial charge transfer. In addition, relevant studies have shown that iron-based catalysts with specific crystal structures can effectively regulate their surface active sites and catalytic activities.

Using a spatially limited topochemical transformation procedure, Zhong *et al.* created a variety of 2D carbon-coated Fe_xSe_y NSs made of various structural crystals (2D Fe_xSe_y@C NSs).¹⁵ The catalytic activity of 2D Fe_xSe_y@C NSs for persulfate activation, which demonstrated the most active performance with a maximum rate (100% with 20 min) and k_{obs} (0.169 min⁻¹), is determined by the crystal structure and the spin state of the Fe active center, which are closely related to the physicochemical properties of Fe_xSe_y in an Fe–Se system. The high Fe spin-state with a large effective magnetic moment is favorable for the interaction between Fe and persulfate, and enhances the delivery of spin-oriented charges, improving the binding energy of persulfate and promoting the decomposition of persulfate. Furthermore, the reactivity of Fe in 2D FeSe₂@C NSs is greater because of its larger electron supply capacity during oxidation and higher 3d charge transfer efficiency (Fig. 1(a)). Moreover, the stability assessments of 2D FeSe₂@C NSs in the diatrizoic acid (DTZ) degradation showed maintained high efficiency through four consecutive cycles. A critical factor contributing to attenuated catalytic performance in such systems is the irreversible adsorption of organic intermediates, which often occurs *via* chemisorption onto active surface sites, thereby blocking further catalytic reactions. The slight performance decline was ascribed primarily to the coverage of active sites by degradation intermediates rather than catalyst deactivation, as evidenced by the restored degradation efficiency after ethanol washing. These results further confirm the structural robustness and recyclability of the 2D FeSe₂@C NS catalytic system.

2.2 Construction of core–shell structures

The aggregation, leakage, and unsatisfactory efficiency of iron-based nanoparticles have limited the activation of persulfate, and the development of core–shell structures has become a hotspot for research of persulfate activators.¹⁶ This means that iron-based nanoparticles are encapsulated in nanostructures, and their structures can be designed and optimized at the nanoscale, showing unique characteristics and advantages. In the process of forming the core–shell structure, new interfacial and electronic properties can also be given to the material, making its application more attractive. For instance, the chain mail catalyst architecture developed by Deng *et al.* demonstrates that the catalytic activity of iron-based nanoparticles can be substantially improved by transferring electrons from the encapsulated metal to the chain mail layer, while promoting distinct catalytic activity on the outer surface.^{17,18} Furthermore, this encapsulation structure can shield the active iron-based core from degradation or aggregation by preventing contact between the active iron-based core and the reaction medium, increasing the catalytic stability.¹⁹ For core–shell catalysts, performance optimization in practical applications is predominantly dependent on precise control of the chain mail structure parameters, among which layer thickness

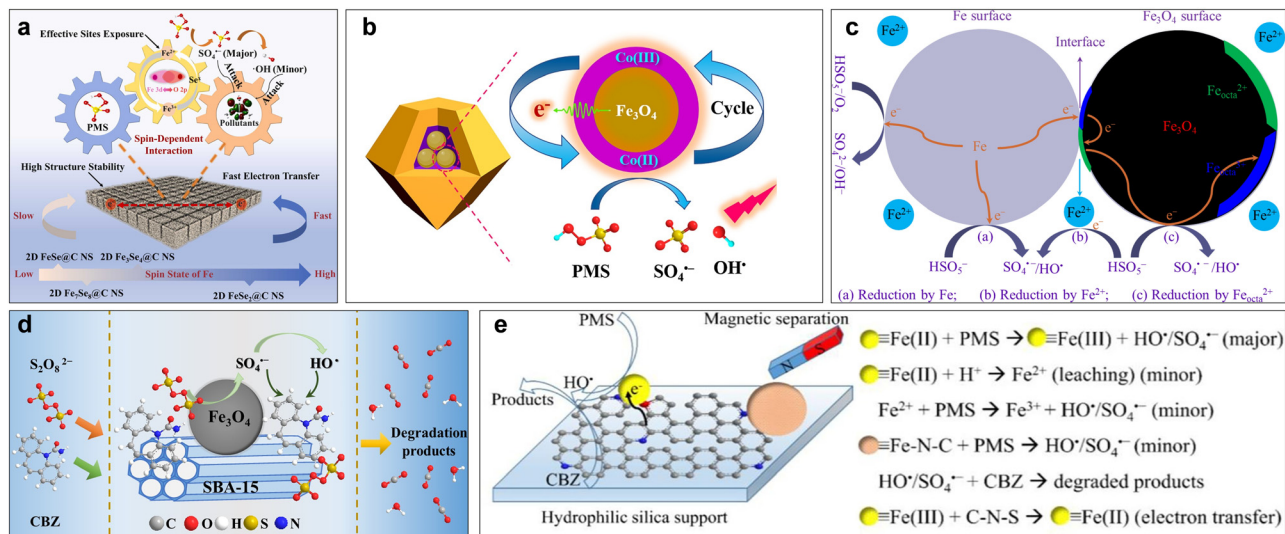


Fig. 1 (a) Catalytic mechanisms of active center spin-dependent catalysts for PMS activation. Reproduced with permission from ref. 15. Copyright 2023 Elsevier. (b) The possible degradation mechanisms of CBZ in the Fe₃O₄@Zn/Co-ZIFs/PMS system. Reproduced with permission from ref. 22. Copyright 2020 Elsevier. (c) Electron transfer in the Fe/Fe₃O₄ composite catalyst during persulfate activation. Reproduced with permission from ref. 27. Copyright 2021 Elsevier. (d) Proposed mechanism of Fe₃O₄@SBA-15 catalyzed persulfate oxidation of CBZ. Reproduced with permission from ref. 28. Copyright 2021 Elsevier. (e) Proposed mechanism of Fe@C-N-S@SBA-15 catalyzed persulfate oxidation of CBZ. Reproduced with permission from ref. 32. Copyright 2022 Elsevier.

constitutes a critical design factor. Although an overly thick encapsulation layer may introduce diffusion limitations that compromise reactant access to active Fe sites, a suitable thickness can markedly enhance interfacial electron transfer.²⁰ Moreover, the closed spatial environment by the core-shell structure not only facilitates the dispersion of active metal species but also effectively inhibits metal particle agglomeration, thereby establishing optimal conditions for catalytic performance enhancement.²¹ In general, a core-shell construction means that there is no moveable internal space and the core and shell are in close contact. Lai *et al.* synthesized a core-shell structure magnetic zeolitic imidazolate framework (Fe₃O₄@Zn/Co-ZIF) by a simple solvothermal method.²² Fe₃O₄@Zn/Co-ZIF displayed exceptional catalytic ability to activate PMS for the degradation of carbamazepine (CBZ). This phenomenon can be attributed to the Fe₃O₄@Zn/Co-ZIF possessing exceptional electron transfer capability. Moreover, the high conductivity of the Fe₃O₄ core is able to speed up the charge transfer and function as an electron donor to encourage the cycling of Co³⁺ to Co²⁺, which will then react with PMS to produce ROS (Fig. 1(b)). The catalyst demonstrated excellent universal applicability, achieving comparable CBZ degradation efficiency in tap water to that observed in deionized water. The observed reduction in degradation rate constant in river water can be attributed to the interference by natural ions and dissolved organic matter in the complex aqueous matrix. Notably, the Fe₃O₄@Zn/Co-ZIF maintained consistently high degradation efficiency across various organic pollutants, confirming its potential as an effective heterogeneous catalyst for water treatment applications. Besides, the researchers created a

new structure with interior space by partially moving the shell or core, which is named the yolk shell structure and referred to as the structure of the active metal core@void@shell.²³ There are many accessible active sites because of the yolk-shell structural cavities that exist between the core and shell. These cavities significantly expose the outer surface of the active metal core.²⁴ This special spatial confinement effect is conducive to improving catalytic performance, and the continuous exposure of active sites can be achieved by using this reactor.²⁵ The diffusion performance is improved in the close-fitting pores because the reactant molecules easily and violently collide with the pore wall and then reflect through the cavity after entering the core-shell structure. Consequently, the space environment of the core-shell structure enhances physisorption energy while also altering catalytic behavior, thus improving the catalytic efficiency throughout the degradation process. Under the limitation of structure, the generated ROS can easily react with the organic pollutants adsorbed nearby, and the migration distance of ROS is significantly reduced, which leads to the enhanced degradation of organic pollutants. Inducing van der Waals forces and increasing electron transfer between the internal structure of the catalyst and the PMS molecules, the core-shell configuration ensures a rise in catalytic efficiency.²⁶

2.3 Introduction of support materials

The incorporation of support materials to disperse iron-based catalysts on various supports not only solves the shortcomings of easy aggregation of traditional iron-based catalysts, but also promotes the development of synergistic

catalysis between iron-based components and supports, improving catalytic efficiency. Additionally, promotion was acquired *via* electron conduction throughout the process. Studies have demonstrated that a variety of metal oxides can directly activate persulfate, effectively degrading a range of pollutants in the water environment, and they also serve as reliable supports for iron-based components. For instance, Hu and co-authors have designed a composite iron corrosion product (named Fe/Fe₃O₄) that exhibits significant catalytic activity towards iopamidol (IPM) and atrazine (ATZ), with corresponding pseudo-first-order rate constants of 1.47 and 1.03 min⁻¹, respectively.²⁷ This study demonstrates that the Fe/Fe₃O₄ composite catalyst facilitates quicker interfacial charge transfer rate and exhibits reduced diffusion resistance compared to a single iron catalyst, allowing for more effective electron transfer to persulfate and resulting in the production of ROS. The catalytic reaction process not only involves the transfer of electrons from the Fe and Fe₃O₄ on the surface of Fe/Fe₃O₄ to persulfate but also includes electron transfer during the Fe(II)/Fe(III) conversion process (Fig. 1(c)). Similarly, molecular sieves serve as an inexpensive support for loading transition metal iron to activate persulfate, due to their unique structural characteristics. Huang and colleagues successfully prepared Fe₃O₄-wrapped SBA-15 (named Fe₃O₄@SBA-15) and achieved a removal efficiency of approximately 100% for CBZ within 30 min.²⁸ Kinetic studies have revealed that the incorporation of support materials significantly enhances the adsorption of persulfate and organic pollutants on the catalyst surface, further promoting the catalytic reaction. On the other hand, highly dispersed Fe₃O₄ also facilitates the activation of persulfate, and the synergistic function of the enhanced adsorption and higher dispersion promotes the production of ROS, which speeds up the removal of pollutants (Fig. 1(d)). It is worth noting that metal organic framework (MOF) materials serve as excellent supports for loading the Fe element, and have been applied to activate persulfate degradation of severe toxic pollutants.²⁹ The iron-based MOF composite catalyst has the advantages of good chemical properties, adjustable structures, and expansive specific surface areas.³⁰ The variable valence of Fe(II)/Fe(III) serves as an effective driving force for the catalytic behavior of the iron-based MOF composite catalysts, and the number of mesopores and specific adsorption often enable them to exhibit better catalytic activity. Yang *et al.* investigated the removal of original pollutants by Fe-MOF-derived carbon with persulfate.³¹ At a catalyst dosage of 0.33 g L⁻¹ and a persulfate concentration of 2 mM, the batch experiments showed the best degradation, degrading almost 80% of trichloroethylene in less than 60 min. According to this study, by enhancing the electron structure and electrical conductivity of catalysts, graphitic N improves electron transfer from persulfate to catalysts, whereas Fe atoms readily couple with pyridinic N to generate Fe-N_x active sites. Consequently, Fe-MOF-derived carbon is a great

catalyst for persulfate activation due to the synergistic effects of Fe and N-doped carbon.

2.4 Incorporation of new components

In addition to increasing adsorption and enhancing the dispersion of active components, doping with non-metal elements is also a strategy worth exploring. In particular, heteroatom-doped carbon materials exhibit a unique electron transfer mechanism and can also be used independently to activate persulfate for pollutant degradation. Incorporating this component can alter the electronic structure and bandgap position of the iron-based catalyst, and even lead to a reconstruction of its catalytic performance. Based on previous work, Wang and colleagues designed an innovative ordered mesoporous material (named Fe@C-N-S@SBA-15).³² This optimized composite material demonstrates excellent performance in the degradation process of pollutants, with which CBZ can be completely degraded within 25 minutes. Within the Fe@C-N-S@SBA-15 structure, the nano Fe provides a rich interface of ≡Fe(II) sites, and the C-N-S component promotes electron transfer, thus optimizing the redox cycling of Fe species. Additionally, the hydrophilic SBA-15 support further aids in facilitating dispersion in water and mass transfer. Particularly in the C-N-S component, doping with N and S species increases the charge and spin density within the carbon framework, promoting electron transfer and the Fe(II)/Fe(III) cycle, thereby achieving a sustained activation effect of persulfate. In addition, the close contact of each component in the composite catalyst encourages the development of interfacial Fe-N-C sites, which helps to activate persulfate to produce ROS as well (Fig. 1(e)). Regardless of the support materials used, the activation of persulfate is crucial, and the key to increasing the catalytic reaction rate is to accelerate the O-O bond cleavage of persulfate to generate active free radicals. DFT calculations demonstrate that the essence of catalysis is to improve the binding ability of the catalyst with persulfate. In the study by Yu and co-authors, an electron-rich nano Fe⁰/FeS heterostructure integrated within thin-bedded graphene (named Fe⁰/FeS/C) has been designed *via* soft carbon-assisted flash joule heating.³³ In this work, Fe⁰/FeS/C degrades chloramphenicol (CAP) through the catalytic activation of sodium persulfate, with a removal efficiency that reaches up to 94.1% within 75 minutes. DFT research results indicate that compared with the adsorption systems of FeS/C or Fe⁰/C with persulfate, the Fe⁰/FeS/C heterostructure is more likely to adsorb persulfate, and due to the improved electron transfer capability, it breaks the O-O bond to produce more free radicals to enhance catalytic activity (Fig. 2(a-c)). The electron-rich Fe₀/FeS/C presents a reduced energy barrier for O-O bond cleavage, and the catalytic process is characterized by a lower Gibbs free energy (-0.58 eV). The electron delocalization effect enables the electron-rich Fe⁰/FeS/C to spontaneously and more easily activate persulfate. The thin-layer graphene in the Fe⁰/FeS/C composite catalyst improves

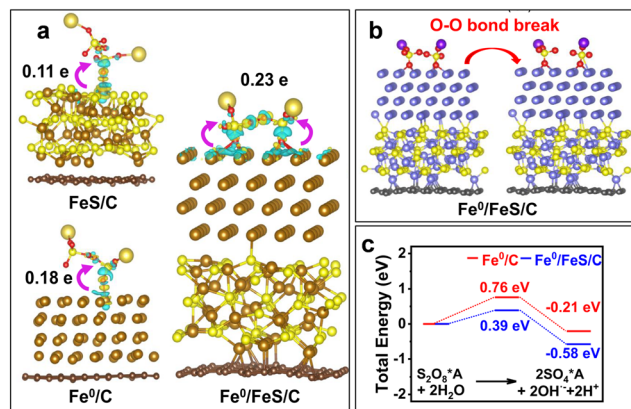


Fig. 2 (a) The electron density difference of persulfate adsorption on FeS/C, Fe⁰/C, and Fe⁰/FeS/C, respectively. (b) The O–O bond breakage process of persulfate on Fe⁰/FeS/C. (c) The free energies for persulfate activation by Fe⁰/C and Fe⁰/FeS/C on the Fe sites. Reproduced with permission from ref. 33. Copyright 2023, Spring Nature.

the electron transfer capability, increasing the efficiency of the catalytic reaction. The active component in the studied composite catalyst consists of the electron-rich nano Fe₀/FeS heterojunction, which spontaneously transfers electrons based on the difference in work function, facilitating the activation of persulfate on the surface for the recalcitrant organic removal.

3. Exploration of mechanisms

3.1 Radical oxidation pathways

Many studies mainly demonstrate that the iron-based composite catalysts promote the electron transfer process between catalytic active components and persulfate through various design improvements. The electrons transferred degrade organic pollutants by disconnecting the O–O in persulfate to generate ROS, including sulfate radicals, hydroxyl radicals or superoxide radicals. The corresponding degradation pathway is radical oxidation.³⁴ The Fe in iron-based composite catalysts generally played an important role in the electron transfer between active sites and persulfate in the production of SO₄^{•-}. The reactions that took place between it and two distinct persulfates were explained by eqn (1) and (2). After further reacting with H₂O, the generated SO₄^{•-} formed [•]OH (eqn (3)), which in turn co-oxidized the original pollutants (eqn (4)).³⁵ The radical generation predominantly depended on the electron transfer across the surface of the catalyst. Consequently, various design improvements aimed at improving the ability of iron-based catalysts to degrade organic pollutants involve increasing the number of active sites for the reaction, reducing electron transfer resistance, and providing a larger specific surface area.



3.2 Non-radical oxidation pathways

However, other studies have found that many similar iron-based composite catalysts may also induce a variety of non-radical pathways, including singlet oxygen (¹O₂), direct electron transfer, and reactive hypervalent metal, or both oxidation pathways may coexist simultaneously. The difference in degradation pathways is contingent upon several factors, such as the active catalyst site, the type of oxidizer, the reaction conditions, and the reaction rate with the target pollutants. In particular when the non-free radical pathway has stronger selectivity and resistance to environmental factors, further exploration of how to enhance the non-radical pathway for degrading organic pollutants is warranted. Zheng and co-authors have inserted iron oxide into ZIF-67 and UiO-66 to form the composite (named MZU) and selected phenylphosphinic acid (PPOA) as the target pollutant to efficiently remove organophosphorus pesticides, with the removal rate being close to 100% within 30 minutes.³⁶ By accelerating electron transfer through carbon induction, heteroatom induction, variable valence metal induction, and other ways, the iron-based MOF composite catalyst may generate more active free radicals quickly and use the free radical pathway to degrade pollutants. In this process, it is found that active free radicals can simultaneously generate ¹O₂ in the form of self-decomposition through excess electrons, and the rapid electron transfer leads to the more generation of ¹O₂, indicating the utilization of both free radical and non-free radical pathways in the degradation of PPOA (Fig. 3(a)). Li and co-authors used Fe(III)-doped g-C₃N₄ (named CNF) as the catalyst, no highly oxidative radicals are detected in reaction process, indicating that the degradation pathway for organic pollutants is a non-radical oxidation pathway, and finally found that the reactive-hypervalent metal ≡FeV=O is the main reactive substance in the activation system.³⁷ In this process, the persulfate first combines with Fe(III) coordinated with N ligands to produce ≡FeV=O, then undergoes an effective degradation reaction with *p*-chlorophenol (4-CP) through electron transfer (Fig. 3(b)), and it is known that the electrons transfer from the iron-based catalyst to persulfate. Notably, Duan and co-authors also have designed a catalyst by anchoring single Fe atoms onto g-C₃N₄ (named SAFe-CN), which completely removes *o*-phenylphenol (OPP) within 30 minutes.³⁸ DFT calculations reveal that the electron density is concentrated in the Fe–O₂ bonding. Partial electron depletion at the O–O bond prevents immediate bond cleavage, with the subsequent electrons being transferred from the Fe–O₂ bond to the O–O bond after the Fe–O₂ bond receives the electrons of the organic pollutant. Compared with the free radical pathway of Fe nanoparticles alone, the SAFe-CN serves as an excellent electron donor, and the isolated single Fe atom in g-C₃N₄ dramatically increases the chemical activity. This enhancement is attributed to facilitated electron transfer and modified electron

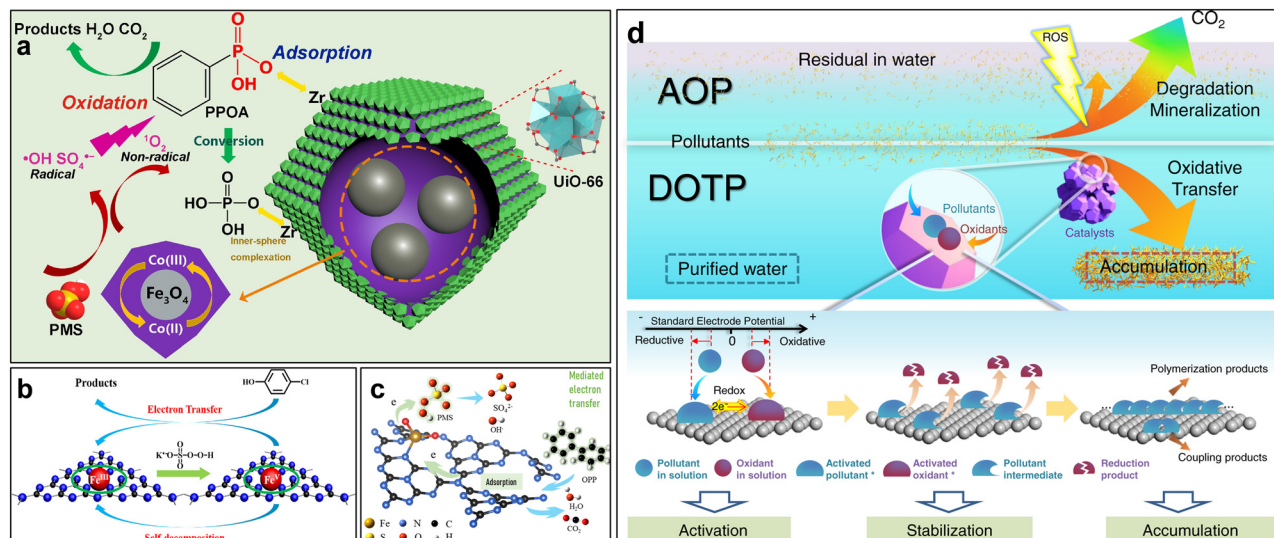


Fig. 3 (a) Electron transfer mechanism of OPP degradation in the persulfate/SAFE-CN system. Reproduced with permission from ref. 36. Copyright 2021 Elsevier. (b) Proposed mechanism of 4-CP degradation in the persulfate/CNF system via a reactive hypervalent metal. Reproduced with permission from ref. 37. Copyright 2018 American Chemical Society. (c) Schematic diagram of the synergistic radical oxidation and non-radical oxidation in the MZU/PMS system. Reproduced with permission from ref. 38. Copyright 2023 Elsevier. (d) The surface (heterogeneous nanocatalyst) functions (i.e., activation, stabilization, and accumulation) of DOTP and the comparison with AOP for water purification. Reproduced with permission from ref. 39. Copyright Spring nature.

distribution, demonstrating a promoted catalyst-mediated electron transfer mechanism (Fig. 3(c)). Persulfate is activated on the catalyst surface through this mediated electron transfer mechanism.

At the same time, Zhang *et al.* found the electron equivalent non-conservation contradiction in the persulfate-based heterogeneous catalytic system, and the electron equivalent consumed by the persulfate is significantly less than the donated electron equivalent from the pollutant.³⁹ In light of this contradiction, the direct oxidation transfer process (DOTP) of removing pollutants from water by heterogeneous catalytic oxidation is first revealed.^{40,41} DOTP involves a double electron redox reaction between pollutants and oxidants on the heterogeneous catalyst surface. In the process, the catalyst surface stabilizes the resultant pollutant intermediates, which then undergo a spontaneous surface polymerization or coupling reaction. The resulting products are then enriched on the catalyst surface (Fig. 3(d)). The catalyst surface plays a crucial role in DOTP, providing a site for electron transfer. At present, reports on DOTP mediated by iron-based materials are few, and more attention is paid to the polymerization process of organic matter. Therefore, rapid electron transfer plays a crucial role in different oxidation systems. Selecting appropriate active sites on the surface of iron matrix composites might be pivotal in directing the various oxidation pathways.

4. Conclusions and perspectives

In summary, regardless of the degradation of organic contaminants by a free radical oxidation pathway or non-free radical oxidation pathway, the interfacial electron transfer

capability of heterogeneous iron-based composite catalysts is crucial, among which the efficiency depends on the resistance controlling the migration of charge carriers within the catalyst. The activation process fundamentally involves electron transfer *via* adsorption-formed connections, including the activation of both pollutants and oxidants. The potential difference serves as the primary driver in the electron transfer process, characterized by an imbalanced potential distribution that leads to the generation of electron absorption and donation, thus initiating electron transfer. Therefore, accelerating electron transfer is a fundamental improvement measure to enhance the degradation efficiency of catalysts, which can be systematically investigated through conventional characterization techniques such as CV and EIS. Advanced characterization approaches including Kelvin probe force microscopy (KPFM), surface photovoltage microscopy (SPVM), and *in situ* zeta potential visualization techniques provide novel dimensions for elucidating electron transfer mechanisms at nanoscale resolution. Nevertheless, this aspect has received limited attention up until now. Enhancing the catalytic interface charge transfer through catalyst modification and changing the oxidation pathway of the reaction system offer promising avenues to achieve enhanced catalytic activity. In this process, it is essential to explore the activation reaction mechanisms of various heterogeneous iron-based composite catalysts, including an examination of activation mechanisms, their combinations, and the conversion of activation pathways.

Despite the promising advancements in understanding the relationship between catalyst structure and components, the type of active substances, and the selective degradation of pollutants, there are still some disadvantages and challenges

that need to be faced and overcome. Firstly, by meticulously controlling the synthesis of iron-based composite materials, it is possible to adjust their composition and structure. The changes in active sites in actual iron-based composite catalysts, which lead to changes in active species, reversal of reaction mechanisms, and even the selective degradation mechanism of target pollutants, clarifying the active sites and the potential interactions between different active sites, are the biggest challenges for further research on the degradation mechanism of iron-based composite catalysts for pollutants. Secondly, there may be interference and potential misidentification information in complex water quality chemical reactions. This necessitates the combination of various identification methods, fully considering the system's reaction conditions, and carefully considering the identification process to avoid interference. Thirdly, since the aqueous phase system used to study the reaction of organic pollutants is a diluted solution system and the concentration of the pollutants is typically in the order of mg L^{-1} , additional methods are required for both qualitative and quantitative analysis of products and paths as well as equilibrium calculation in order to guarantee the validity of testing results. Fourthly, most research to date has been confined to "beaker experiments" in the laboratory, lacking research on the degradation of pollutants in actual complex polluted environmental areas and the evaluation of application value. In subsequent research, attention should shift from continuous batch experiments to the actual wastewater treatment of polluted sites to achieve an intelligent feedback response between wastewater quality and reactant dosage. In addition, although many researchers have deeply studied the optimal performance of persulfate activation and the removal of pollutants by iron-based composite materials, the stability and lifespan of iron-based composite catalysts under actual conditions are critical in determining treatment costs. Establishing a robust evaluation system for both the catalytic performance and cost-effectiveness of iron-based catalysts is key to achieving engineering applications. To accomplish this goal, it is essential to uncover the detailed deactivation mechanisms and engineer more robust catalysts to achieve rapid degradation and mineralization of pollutants. Specifically, this can be accomplished through the integration of computational simulations and machine learning algorithms to establish quantitative "composition–structure–activity" relationship models. These predictive models, trained on multidimensional datasets encompassing synthesis parameters, structural descriptors, and performance metrics, can provide intelligent guidance for customized high-throughput (HT) computational screening or experimental tests, thereby enabling the intelligent design and performance prediction of catalytic materials. Finally, environmental issues related to the activation of persulfate systems by iron-based composite catalysts need to be noted, including the production of toxic by-products, the disposal of unreacted persulfate, and the potential impact of residual catalysts on organisms. Regulating the oxidation mechanism

through strategy adjustments can reduce the production of toxic by-products, especially the precise regulation of radical ($\text{SO}_4^{\cdot-}$) to non-radical ($^1\text{O}_2$) pathway ratios can substantially mitigate hazardous by-product formation. A comprehensive multilevel toxicity assessment framework should be implemented, incorporating identification of degradation intermediates *via* liquid chromatography-mass spectrometry/mass spectrometry analysis, computational toxicology prediction using quantitative structure–activity relationship (QSAR) models (*e.g.*, ECOSAR and T.E.S.T.), and acute toxicity tests. Treatment options for persulfate include targeted removal of sulfate ions in treated water or investigating high-value sulfate conversion to make advantageous use of the created sulfate. Continued advancements in the understanding and application of iron-based composite catalysts will greatly benefit the field of heterogeneous transition metal catalysis and are expected to play a significant role in solving global environmental pollution as well as the energy crisis.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this perspective.

Author contributions

Lu Huang: writing – original draft. Weigang Zhu: writing – review & editing, conceptualization. Yunxin Wu: writing – review & editing, validation. All authors read and approved the final manuscript.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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