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Progress in oxidative polymerization: Advancing resource recovery through polymerization pathways

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Abstract: When treating wastewater, traditional AOPs mainly break down pollutants into harmless substances completely with radical chain reactions. However, the long-term use of these methods brings problems in sustainable development. They use too much energy and produce large amounts of carbon emissions. Researchers have carried out recent studies on oxidation-polymerization ways. These studies show that polymerization reactions work better than mineralization processes. They can remove organic pollutants effectively. They also cut down energy use greatly and help realize the reuse of resources. This paper summarizes the working principles and newest progress of polymerization reactions. These reactions are started by different active substances. The content includes radical ways like organic and inorganic radicals. It also includes non-radical ways such as high-valent metal oxides, electron transfer processes, complexes and singlet oxygen. Additionally, this paper puts forward methods to improve polymerization reactions. These methods come from two aspects. One is radical ways including concentration synergistic regulation, redox potential and nanoconfinement. The other is non-radical ways including electron regulation, microstructure regulation and composite carrier design. Finally, this paper talks about the difficulties and limits of polymerization ways in removing organic pollutants and lists future research directions in this area. It aims to offer reference and theoretical help for the later use of oxidative polymerization ways in resource recovery.

Key words: Oxidative polymerization; Resource recovery; Advanced oxidation process; Wastewater treatment

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1. Introduction

Currently, pathogenic microorganisms and harmful contaminants present in aquatic environments pose serious threats to both human health and ecological security; consequently, water quality and safety have direct implications for ecological stability and the advancement of human civilization[1-3]. With the accelerating pace of modern industrial and agricultural development, water pollution has intensified. The resulting deterioration of water quality not only aggravates the global freshwater crisis but also emerges as a critical barrier to sustainable societal development[4-6]. Within existing water treatment systems, chemical oxidation —a conventional yet essential technology—plays a pivotal role in controlling water pollution. This approach typically relies on strong oxidants to mineralize organic contaminants into carbon dioxide, water, or other inorganic substances[7-12]. However, traditional chemical oxidation processes have long prioritized pollutant removal efficiency, often overlooking the substantial external energy input required. This imbalance between energy consumption and the energy released during degradation can lead to significant resource waste. In response, technological innovation is now driving a paradigm shift in water treatment, transitioning from single-objective pollution removal to integrated matter-energy management. This strategy wants to make water quality better and get energy back by using related technologies. These technologies help turn pollutants into useful things and treat water with low carbon[13-15]. Advanced oxidation processes (AOPs) are used much in water pollution control. They are among the most effective ways. They break down toxic things in wastewater[16-18]. AOPs function primarily by generating reactive oxygen species (ROS) in situ, which transform harmful compounds into non-toxic or minimally toxic products. These reactive oxygen species encompass a wide range of oxidizing agents, generally categorized into radical species (e.g., sulfate radicals, hydroxyl radicals) and non-radical species (e.g., singlet oxygen, high-valent metal-oxo species). Their reaction mechanisms and pollutant degradation capacities vary significantly depending on the type of ROS involved[8, 19-23].

Studies have demonstrated that, under well-defined reaction conditions, organic contaminants can be oxidatively con-

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verted into transient organic radical species. These radical intermediates subsequently engage in intermolecular coupling reactions, leading to the formation of high-molecular-weight polymeric products. This transformation pathway is generally referred to as oxidative polymerization, representing an alternative pollutant conversion mechanism distinct from conventional mineralization-dominated advanced oxidation processes[24]. As an emerging reaction pathway within advanced oxidation technologies, oxidative polymerization has attracted increasing attention in recent years for the treatment of organic wastewater[25-27]. Unlike traditional AOPs, which aim for complete mineralization, oxidative polymerization selectively transforms soluble organic substrates into valuable solid polymers[28-33]. These polymeric products typically exhibit low solubility, allowing them to be easily separated from catalyst surfaces for potential use in industrial plastic manufacturing or chemical refining processes[27, 34-36]. More importantly, oxidative polymerization introduces a fundamentally new reaction route within conventional advanced oxidation frameworks. Proceeding through either radical or non-radical mechanisms, this process differs from traditional degradation pathways by preserving the carbon skeleton of pollutants while reducing external energy input, thereby retaining the embedded chemical energy and achieving considerable resource savings. Despite its promising potential for pollutant valorization, significant challenges remain in achieving stable and efficient polymerization-oriented pollutant removal under the complexity of real aquatic environments[24, 37, 38].

This review puts forward a new mode for pollutant transformation. It is different from traditional mineralization methods. It gives a resource recovery path mainly driven by oxidative polymerization. This model breaks away from the old theory that focuses on full degradation. It pays more attention to high-value conversion of pollutants with polymerization reactions. Earlier reviews have studied many parts of oxidation polymerization. Most of them pay attention to non-radical paths. However, none have given a full and clear comparison between radical and non-radical oxidation polymerization. This is especially true for pollutant degradation and resource recovery. This review makes up for this shortage. It summarizes recent progress of oxidation polymerization in AOP systems. It looks deep into radical and non-radical reaction pathways to explain main active species, polymerization mechanisms and affecting factors (Tables 1 and 2). We also fully discuss key methods used in recent years to improve oxidation polymerization. These methods raise polymerization selectivity, control reaction pathways and speed up polymerization processes. They do so by adjusting catalyst structure, building interface reaction environment and optimizing working conditions. These methods deepen understanding of basic oxidation polymerization mechanisms. They also offer important guidance for building controllable and large-scale polymerization-based pollutant transformation technologies. This review is the first systematic and in-depth work that combines these mechanisms. It builds a unified frame for radical and non-radical pathways and brings special value to the whole field. This review also looks into future use of oxidative polymerization in water treatment and resource recovery. It shows its chances and difficulties in developing green chemistry. It helps cut carbon emissions and realizes high-efficiency resource use of pollutants. We hope this review offers theoretical support and research ideas to support the building of next-generation low-carbon and high-efficiency water treatment technologies.

2. Radical pathways in oxidative polymerization

In advanced oxidation systems, the radical pathway is a key mechanism for pollutant degradation. ROS drive this process and help turn pollutants into polymeric products. Generated radicals fall into two groups according to chemical features. They include inorganic radicals (e.g., hydroxyl radicals, sulfate radicals) and organic radicals (e.g., acetylperoxy radical, CH_3CO_3•). Most AOPs studies pay attention to inorganic radicals at present. Organic radicals lack sufficient research attention. Especially for acetyl peroxy radical and its role in pollutant polymerization reactions, the situation is even more so. This study explores the formation mechanism of CH_3CO_3• and its role in polymerization reactions. It compares the reaction characteristics of the two types of free radicals and provides theoretical support for the application of organic free radicals in water treatment.

2.1. Mechanism of inorganic radical-mediated oxidative polymerization

In AOPs, reactive oxygen species are essential for the destruction of pollutants via radical processes. Radical-induced mineralization is usually seen as the main pathway. It tends to bring about the generation of oligomers. Such findings show oxidative polymerization may take place together with radical-driven degradation. They offer new views on how environmental conditions affect pollutant transformation processes.

2.1.1. Inorganic radical oxidation polymerization pathway

In advanced oxidation processes, sulfate radicals (SO_4•$^-$) and hydroxyl radicals (•OH) serve as primary inorganic radical, efficiently removing pollutants through redox reactions[11, 39-41]. Although oxidants can eliminate pollutants in their unactivated form, their restricted radical production efficiency impedes comprehensive pollutant degradation [42-44]. Therefore, activation techniques are essential to promote sustained radical generation, thereby enhancing pollutant degradation efficiency.

In inorganic radical-mediated pollutant conversion, mineralization is typically the main transformation pathway, requiring external energy (e.g., photoactivation[45], pyrolysis[46], or ultrasonic radiation[47]) to provide activation energy. This induces peroxide bond cleavage and generates ROS like SO_4•$^-$ and •OH[48], which break down the carbon skeleton of pollutants, ultimately converting them into CO_2, H_2O, and inorganic ions[8]. In PS-based oxidation systems, the oxidant concentration and ROS generation significantly influence the process. Sufficient ROS lead to complete mineralization, while insufficient ROS result in the formation of radical cations (e.g., phenol radical cation HO−Ph•+) that undergo polymerization to form dimers or oligomers[24, 49, 50]. The polymerization products formed can be effectively captured using physical separation techniques such as precipitation or filtration, offering a novel approach for both pollutant remediation and resource recovery[51-54]. Thus, SO_4•$^-$ and •OH not only mineralize pollutants but also facilitate polymerization, though typically forming only oligomers. Section 4.1 will detail the thresholds of

ROS adequacy, offering insights for optimizing oxidant use and promoting oxidative polymerization to reduce carbon resource consumption.

2.1.2. Persulfate vs. hydroxyl radical oxidation pathways

In the radical oxidation process, although both SO_4•$^-$ and •OH degrade pollutants through similar mechanisms, their distinct physicochemical properties result in significant differences in their reactivity and overall behavior (Figure 1a). SO_4•$^-$ (oxidation potential 2.5–3.1 V_{NHE})[20] exhibits a higher oxidation capacity compared to •OH (1.8–2.7 V_{NHE}) [20], offering three key advantages: First, SO_4•$^-$ is less pH-dependent. Second, its longer half-life (30-40 μs) contrasts with the much shorter lifetime of •OH (<1 μs)[55]. Third, SO_4•$^-$ exhibits higher selectivity, preferentially attacking electron-rich organic compounds (such as aromatic compounds), whereas •OH tends to undergo non-selective quenching reactions with common anions (e.g., Cl^-, HCO_3^-).[56-59](Table 1).Taking phenol as an example, in SO_4•$^-$-dominant AOPs, single electron transfer (SET) and radical adduct formation (RAF) predominate. In this case, phenol undergoes SET to form a phenol radical cation (HO–Ph •+), while SO_4•$^-$ gains an electron and converts to SO_4^{2-}. In the RAF process, SO_4•$^-$ adds to the benzene ring, forming a carbon-centered adduct, which loses an electron to produce phenoxy radicals through H^+ elimination. In contrast, in •OH-dominant AOPs, the formation of RAF and oxygenation occurs. •OH first adds to the benzene ring to form an adduct, from which phenoxy radicals are generated via water dissociation. Additionally, oxygenation of the adduct forms persulfate radical, leading to oxidative degradation[8].

2.2. Mechanism of organic radical-mediated oxidative polymerization

CH_3CO_3• is a crucial organic reactive oxygen species that is primarily produced from its peroxygenated precursor, peracetic acid (PAA, $CH_3C(O)OOH$)[60-62]. As a strong oxidant and disinfectant, PAA has long been applied across various industrial sectors[63-65]. Recent research points out that PAA owns the peroxy bond like common oxidants. It has multiple benefits in water treatment. These include lower toxicity, higher efficiency, less disinfection by-products and better environmental adaptability[66-68]. Consequently, PAA is gaining increasing attention as an alternative disinfectant in wastewater treatment.

During the activation of PAA, different reactive species can be formed. These include organic radicals (CH_3CO_3•, CH_3CO_2•, •CH_3) and inorganic radicals (•OH, HO_2•)[69]. Among them, CH_3CO_3• shows a key function in pollutant transformation. But Related mechanism research on CH_3CO_3•-mediated oxidation is still very limited[60, 63, 70]. In the conversion of phenol, CH_3CO_3• mainly follows the hydrogen -atom-abstraction (HAA) route, where abstraction at the ortho-site gives rise to phenoxy radicals (PhO•). These PhO• species undergo dimerization or cross-coupling reactions to form oligomeric or polymeric products. Further structural changes may include tautomerization, C–O bond breakage, or aromatic ring opening. These steps can lead to more thorough pollutant transformation[70, 71]. PhO• can also react directly with CH_3CO_3• to form radical–radical adducts. These products are metastable and they will finally experience structural rearrangement or bond breakage[72] (Figure 1b). Although CH_3CO_3• has a lower redox potential (E° = 1.60 V_{NHE}) than traditional inorganic radicals like SO_4•$^-$ and •OH. It supports unique transformation pathways. These paths involve C–C bond breakage and aromatic ring destruction[72, 73] (Table 1). Existing studies on inorganic-radical-induced oxidative polymerization is still insufficient. While CH_3CO_3• itself is not strongly electrophilic, the formed phenoxy radicals have stronger nucleophilicity. This combination favors radical polymerization more easily than common inorganic radical systems[72]. Researchers have not confirmed whether inorganic radicals have higher or lower polymerization tendency than organic radicals. Therefore, more comparative mechanism studies are needed in future work.

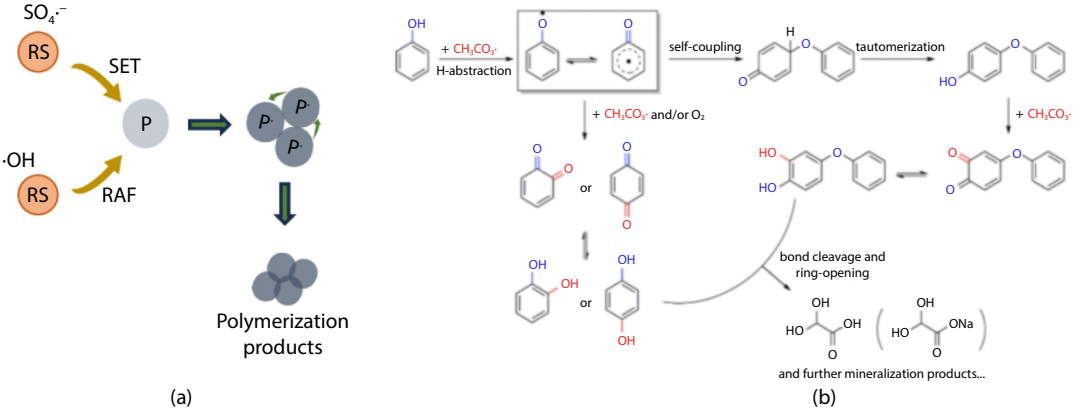

Fig. 1. (a) Inorganic radical (SO_4•$^-$ and •OH) oxidative polymerization pathway. (b) Organic radical (CH_3CO_3•) oxidative polymerization pathway. Reproduced with permission[72]. Copyright 2022, Elsevier.

Table 1. Comparison of the Key Properties of Organic and Inorganic Radicals

Typology	Organic radical	Inorganic radical	
Typical example	CH_3CO_3•	SO_4•$^-$	•OH
Redox potential	1.60 V_{NHE}[72]	2.5–3.1 V_{NHE}[20]	1.8–2.7 V_{NHE}[20]
Half-life	56μs[74]	30–40 μs[55]	10–3 μs[75]
O-O bond energy	159 kJ mol^{-1} (PAA)[76]	317 kJ mol^{-1} (PS)[76]	213 kJ mol^{-1} (H_2O_2)[11]
Electrophilicity index	2.28 eV[72]	8.55 eV[77]	7.48 eV[77]

They should cover different radical types and various pollutant substrates.

3. Non-radical pathways in oxidative polymerization

Radical-mediated oxidative polymerization is driven by inorganic and organic radicals. Although this approach has been explored in many studies. Most research pays attention to fast pollutant degradation and polymerization initiation. Few works focus on controllable resource conversion and polymer structural tailoring. In contrast, non-radical pathways have attracted increasing research focus in recent years due to their higher reaction selectivity and better reaction stability. These pathways include singlet oxygen, high-valent metal–oxo complexes, surface-bound intermediates and electron-transfer routes (Figure 2). These pathways allow more accurate control of reaction mechanisms and polymer growth progress. To completely use the resource recovery potential of oxidative polymerization, it is necessary to explore the mechanism effects of radical and non-radical pathways in pollutant transformation and polymer structure formation (Table 2).

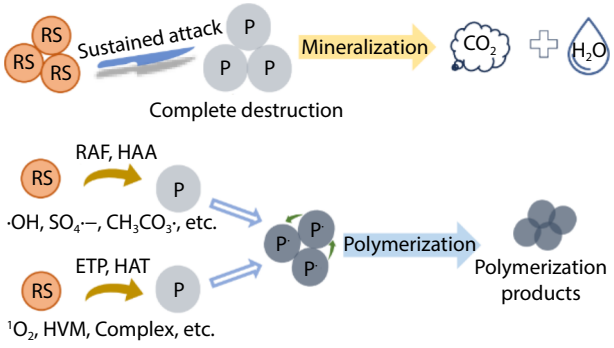

Fig. 2. Schematic of mineralization and polymerization pathways (radical and non-radical reaction mechanisms).

3.1. High-value metals

In non-radical oxidation systems, high-valent metal (HVM)–oxygen species serve as the mian reactive centers. These species oxidize organic contaminants and drive polymerization via electron-transfer (ET) or oxygen-atom-transfer (OAT) pathways. HVM–oxygen intermediates are usually formed from oxidants such as PMS, PDS, or H_2O_2. Their reactivity lies between classical radicals and molecular oxidants. They have strong oxidation ability and also show good selectivity and controllability. When reacting with substrates like phenols, anilines or other pollutants with electron-rich groups, the metal center starts an electron-transfer step. This step produces partially oxidized intermediates including phenoxy radicals or iminium species. These intermediates then take part in intermolecular C–C or C–O coupling reactions. Polymer products can be formed in this process. Radical pathways often show multi-step chain reactions and poor controllability. By contrast, oxidation by high-valent metals shows obvious "site-specific" and "directionall" features. Adjusting the redox cycle and coordination microenvironment of the metal center helps achieve selective control of reaction routes. Moreover, the good regenerability and stable catalytic performance of HVM systems support the conversion from pollutants to resources. Changing the electronic structure of the metal center and improving catalyst–substrate interface interactions can guide the process of oxidative polymerization. It can shift from simple pollutant removal to adjustable structural reorganization. This approach allows organic pollutants to be turned into functional polymer materials. Such a shift from "oxidative degradation" to "functional polymerization" builds a new theoretical framework. It supports the combination of environmental remediation and resource utilization. In later sections, we will further discuss the features of different HVM–oxygen species and summarize the latest progress in this field.

3.1.1. Cu(III)–O

Copper is widely employed in AOPs due to its abundant natu-

Table 2. Comparison of radical and nonradical pathways in oxidative polymerization

Classification	Key active species	Mechanistic features	Strengths	Drawbacks	Common applications
Inorganic radical pathway	SO_4•$^-$, •OH	High oxidation potential; diffusion control enables non-selective oxidation	High reactivity, broad substrate range.	Low selectivity, prone to oxidation, sensitive to pH.	PS-based or Fenton-type systems [20, 49].
Organic radical pathway	CH_3CO_3•	Promote coupling reactions through radical addition or hydrogen abstraction.	Selective toward aromatic compounds	Reduced reactivity; difficulty in controlling intermediates.	Peracetic acid or organic peroxide systems; [70-72].
HVM	Cu, Co, Fe, Ni, Mn	Metal-oxygen group-mediated transfer of electrons or hydrogen atoms.	High selectivity; tunable potential; mild conditions.	Requires precise coordination and control; metal leaching may occur.	Metal-based catalysts initiate PS reactions; phenol oxidation polymerization [24, 53, 125, 145, 199].
ETP	Surface redox site or conductive support	Triggered by interfacial electron transfer; radical intermediates are extremely rare.	Low energy consumption; green manufacturing processes.	The rate is limited by conductivity and charge transfer efficiency.	Carbon-based single-atom catalysts; Electrochemical oxidation polymerization [156, 158].
complex	Metal–pollutant complexes or adsorbed intermediates	Surface-assisted promotion facilitates intramolecular electron transfer and enables polymerization reactions.	High-level surface control; Increased stability; Selective enhancement.	dependent on the surface chemical properties and concentration of active sites.	Metal oxide or MOF catalysts; interface-driven polymerization [90, 125, 171].
$^1O_2$	$^1O_2$	Selective oxidation achieved through electron addition	High selectivity; mild and eco-friendly.	Short lifetime; low yield; substrate-dependent reactivity.	Selective polymerization of phenols and aromatic Amines [178, 191].

ral supply, economical cost and flexible multivalent redox chemistry[78-82]. In peroxide-activated systems (PMS, PDS, H_2O_2), Cu(III)–OH acts as an important high-valent species. It shows strong oxidation ability and stable electron-transfer performance. Cu(III)–OH differs from •OH and $SO_4^{\bullet-}$ in reaction patterns. It realizes substrate oxidation by selective and directional electron transfer instead of radical chain reactions[83, 84]. Cu(III) has a redox potential ranging from 1.57 to 2.3 V and usually presents four or six coordination structures. It is a highly selective but unstable high-valent oxidant that can be easily reduced into Cu(II) or Cu0[83-87]. In peroxide-activated AOPs systems, Cu(III)–OH starts non-radical oxidative polymerization by taking away one electron and one proton from phenols, anilines and other substrates through single-electron transfer (SET). This process forms phenoxy or iminium intermediates[88]. These intermediates then go through Cu(III)–mediated C–C or C–O coupling reactions. They further form oligomers and polymers[53, 89]. Because Cu(III)–OH only causes partial oxidation of pollutants instead of complete degradation, it is more conducive to structural reorganization and polymer generation and provides a feasible way for pollutant valorization. It shows obvious regioselectivity and mainly acts on electron-rich aromatic sites or amino-activated positions, supporting the controlled growth of polymers. It avoids the random and uncontrollable reactions in common radical pathways[90, 91]. Currently, phenol polymerization driven by Cu(III)-OH can produce π-conjugated materials with great potential in functional applications. Such polymers can be used as adsorbents or electrode materials. They also support the realization of functional resource recovery from pollutants[90, 91].

3.1.2. Co(IV)=O

As a strong oxidant with high selectivity, Co(IV) is a key reactive species in advanced oxidation processes. [21, 92-94]. With strong electrophilicity, it can oxidize electron-rich and stubborn pollutants effectively, thereby reducing the toxicity of these pollutants[95]. Because dissolved Co(II) may bring certain environmental risks, Co-based systems often use solid catalysts to reduce the leaching of Co(II)[96-99]. Co(IV)=O species carry out mild and controllable oxidation of organic pollutants. They rely on synergistic electron-transfer or oxygen-atom-transfer pathways. They are more likely to produce polymerizable intermediates rather than complete mineralization products[61, 100-102]. Co(IV)=O is usually formed by the oxidation of Co(II)/Co(III) with external oxidants. With strong electrophilicity, it tends to extract electrons from π-bonds or phenolic hydroxyl groups in organic molecules, generating phenoxy radicals bound to the surface. These radicals do not spread into the bulk solution. This is different from common radical systems. They provide directional coupling on the catalyst surface. This process realizes controlled polymerization reactions[89, 92, 103]. The Co(IV)=O pathway also shows obvious substrate specificity and adjustable performance[71, 104-106]. Liu *et al*. found that the ionization potential (IP) of substrates affects the reaction degree greatly. Substrates with IP lower than about 6.0 eV can be oxidized easily. Substrates higher than this value show weak reactivity. This proves the importance of reasonable substrate selection[61]. Wang *et al*. confirmed that Co_3O_4 can activate peroxydisulfate (PS) through a non-radical mechanism. The activated O–O bond captures hydrogen from phenol to generate organic radicals. These radicals polymerize into insoluble substances later[107]. Co_3O_4 with different shapes has different catalytic effects. Rod-like Co_3O_4 (110) has the highest activity. This shows that surface structure plays a key role in oxidation-induced polymerization[107]. These research results can provide effective guidance for the development of oxidative polymerization pathways.

3.1.3. Fe(IV)=O

Iron ranks as the fourth most abundant metal in the Earth's crust. It owns good environmental compatibility, low cost and flexible redox chemistry from Fe(II) to Fe(VI). These features support its wide application in AOPs[43, 44, 108, 109]. Fe(IV)=O is a typical high-valent iron species. It acts as a green, efficient and selective oxidant. It has a long lifetime of 7-10 s. It also holds high steady-state concentration and good oxidant utilization efficiency[110-112]. Recent studies prove the function of Fe(IV)=O. It can realize highly selective transformation of phenolic contaminants. Fe(IV)=O oxidizes phenols into phenoxy radical intermediates through electron-transfer pathway. These intermediates then undergo intermolecular self-polymerization driven by π–π stacking. About 90% of pollutants are converted into high-molecular-weight polymers. This method achieves efficient organic-carbon recovery. It also produces valuable precursors for fine chemical production[113, 114]. In comparison to •OH, ($E^0 \approx 2.8$ V), Fe(IV)=O demonstrates a more moderate redox potential ($E^0 \approx 1.0$-1.5 V)[24]. It allows controllable electron transfer, avoiding excessive mineralization of pollutants[115]. Theoretical studies give further confirmation that Fe(IV)=O tends to take part in electron-transfer reactions. It does not prefer direct oxidation. This effect helps stabilize radical intermediates and promote the following polymerization processes[116]. This finding breaks through the treatment mode of traditional advanced oxidation technology with the goal of complete mineralization. It provides a theoretical basis for building new catalytic systems. Such systems realize the synergy of "pollution control and resource conversion". It shows important application potential in organic waste resource utilization.

3.1.4. High-valent Mn

Mn is a fourth-period Group VII.B element. It has low cost, low toxicity, good environmental compatibility and multiple oxidation states (Mn(II)–Mn(VII)). It also has flexible multielectron redox properties and various crystal-field effects. These traits support different oxidation effects in advanced oxidation processes[117-122]. MnOx catalysts can activate persulfates with high efficiency. They boost pollutant oxidation through electron transfer or hydrogen abstraction. This process forms organic radicals that then take part in polymerization reactions[123, 124]. Research results show that MnOx surfaces build efficient and directional transformation pathways in acidic conditions. Pollutants are adsorbed in a selective way. They are oxidized via electron transfer to form surface-bound radicals. And Mn(IV) is reduced into Mn(III) at the same time[125]. Synthesis methods and crystal structures of MnOx affect the exposure of Mn active sites. They decide the degradation efficiency and main reactive species in MnOx/PS systems[125-130]. In MnO_x/PMS systems, phenol degradation follows such an order: γ-MnO_2 > β-MnO_2 > α-MnO_2 > Mn_2O_3 > MnO. MnO shows low activity because it lacks high-valent Mn

active centers[125]. Miao *et al*. also proved that PMS activation follows a Mn(IV)=O–dominated pathway. Mn(IV)=O has a relatively long service life. It oxidizes organic substances into oligomeric intermediates. These intermediates then carry out self-polymerization[110, 131]. This transformation is different from radical mechanisms. It depends on metal-substrate electron coupling, offering high selectivity and supporting controllable polymer growth[125, 131-134]. In general, Mn(IV)=O helps realize selective oxidation and polymerization via confined electron transfer and reversible redox cycling. It offers an efficient and resource-based pathway for non-radical oxidative polymerization[110, 131].

3.1.5. Ni(IV)=O

Nickel, a transition metal in Group VIII of the fourth period, possesses unique electronic configurations that confer high plasticity, thermal stability, corrosion resistance, and strong oxidizing properties[135-139]. In nature, nickel commonly exists as Ni(0), Ni(II), Ni(III), and Ni(IV), with Ni(II) species (such as NiO and $Ni(OH)_2$) being the most prevalent. Among these, Ni(IV) is a particularly potent oxidizing agent[140, 141]. Extensive studies on the NiO/PS system have demonstrated that NiO, acting as a p-type semiconductor with unpaired d electrons, can mediate the selective oxidation of organic substrates to generate active intermediates that catalyze subsequent polymerization reactions[90, 142-144]. In NiO, Ni^{2+} ions readily generate lattice vacancies, causing charge imbalance. During catalytic polymerization, the system promotes the formation of high-valent Ni(IV) through a two-electron transfer process[145, 146]. This strongly oxidizing Ni(IV) center converts organic pollutants into radical intermediates that subsequently initiate surface polymerization[147]. Furthermore, introducing oxygen vacancies (V_O) optimizes electron-transfer pathways, enhances directional electron migration from organics to the catalyst surface, and markedly accelerates oxidative polymerization[145, 146], as discussed in Section 5.2.1. Mechanistic analyses also show that Ni(II) can be rapidly converted into a dynamic Ni(III)/Ni(IV) mixed-valence system via oxidative addition and molecular oxygen. This reversible valence cycling critically regulates C-C and C-O coupling, with Ni(IV) exhibiting particular efficiency in promoting carbon–carbon bond formation[148].

3.2. Electron transfer process

In non-radical oxidation systems, the electron transfer process (ETP) represents one of the primary pathways linking pollutant transformation with subsequent polymerization. Unlike conventional radical mechanisms, ETP avoids short-lived and non-selective radical species, instead enabling mild oxidation and directional polymerization through spatially confined interfacial electron exchange. Fundamentally, ETP arises from the electronic coupling between catalyst surface states and the molecular orbitals of pollutants, thereby providing higher energy efficiency and reaction selectivity than radical-based pathways[8, 24, 147]. ETP predominantly occurs at the interfaces of metal-based and carbon-based catalysts[24, 149, 150]. Metal catalysts typically facilitate oxidative polymerization by generating high-valent metal species (Section 3.1) or forming surface coordination complexes (Section 3.3) through electron transfer. In contrast, carbon materials enable highly localized and selective electron transfer that promotes pollutant oxidation and polymerization without forming radical intermediates, offering a sustainable route for resource-oriented pollutant conversion[151, 152]. Benefiting from their intrinsic electronic conductivity, carbon-based catalysts construct efficient electron-transport channels between pollutants and persulfate (PS) oxidants. This charge-transfer bridge substantially decreases interfacial resistance and accelerates electron migration from pollutants to oxidants[39, 153, 154]. Thermodynamically, electrons from adsorbed pollutants are injected into the conduction band or defect states of the carbon matrix and subsequently driven toward PS along surface charge-density gradients, inducing O–O bond cleavage and forming sulfate radicals[155]. Simultaneously, electron loss from pollutants produces organic radicals, which undergo confined surface polymerization. Compared to metal-centered ETP systems, carbon-based catalysts offer metal-free composition, environmental compatibility, and structural tunability, making them highly aligned with principles of sustainable catalysis[156]. Their π-conjugated frameworks, abundant defect sites, and adjustable electronic structures not only promote directed electron flow but also enable selective C–C or C–O coupling while suppressing non-selective radical generation[157]. Moreover, tailoring the surface chemistry of carbon materials —through heteroatom doping, electron-density modulation, or creating composite interfaces with metal oxides—can further enhance the reactivity and adaptability of ETP pathways[158, 159]. Due to this structure–electron tunability, carbon-based ETP catalysts exhibit strong potential for integrated applications in environmental remediation and value-added material synthesis[160, 161].

3.3. Complex

After interacting on the surface, the catalyst and oxidant can form active complexes that play a crucial role in the conversion and polymerization of organic pollutants. First, the oxidant preferentially adsorbs onto active sites on the catalyst surface and synergistically reacts with it to form a reaction complex; Subsequently, this complex catalyzes the oxidation of organic pollutants, activating their structures and converting them into reactive radical intermediates. These intermediates undergo spontaneous polymerization to form stable polymeric products. Due to variations in the structural composition and formation mechanisms of these complexes, their methods of pollutant activation and conversion pathways also differ. The following sections will respectively elaborate on the reaction mechanisms for metal-based catalysts and carbon-based catalysts.

3.3.1. Metal-based catalysts

In non-radical oxidation systems driven by metal–oxidant complexes, the oxidant interacts with the metal oxide surface by replacing surface hydroxyl groups (-OH) and coordinating directly with the metal centers to form reactive complexes. These complexes oxidize the target pollutants without generating radicals, thereby bypassing the conventional radical chain pathway[162]. Within such redox routes, the catalyst surface must maintain an oxidation potential higher than that of the pollutant to sustain the degradation process[156, 163, 164]. When species such as $SO_4^{\bullet-}$, •OH, or $^1O_2$ are produced, they diffuse into the bulk solution, while the interfacial potential remains relatively stable and does not immediately drop during pollutant oxidation[90]. In contrast, during the formation of surface metal–oxidant complexes, the interfacial potential

increases concurrently, enabling the oxidation of adsorbed pollutants[165]. Because these interfacial complexes exhibit moderate oxidative strength, their reactions often proceed through hydrogen abstraction or partial oxidation[35, 107, 145]. For instance, in MnO_x/PMS systems, the complex can extract electrons from phenol and induce dehydrogenation of the phenolic –OH group to form phenoxy radicals. These intermediates may undergo ring-opening and subsequent coupling reactions to yield polymeric products, ultimately achieving pollutant transformation and removal[125].

3.3.2. Carbon-based catalysts

In recent years, non-metallic carbon materials have gained considerable attention in heterogeneous catalysis owing to their diverse allotropic structures and highly tunable electronic and interfacial properties[39, 166]. Their catalytic behavior is governed by the coordinated influence of the carbon framework's microstructure, defect density and distribution, as well as the chemical environment of surface functional groups[39, 167, 168]. In non-radical oxidation systems, the reaction typically initiates with the co-adsorption of oxidants and organic pollutants on the carbon surface. During this stage, the oxidant is activated at specific adsorption sites and forms a reactive carbon–oxidant interfacial complex, which substantially elevates the local oxidation potential (E_{cat})[54, 169, 170]. This activated complex subsequently drives the single-electron oxidation of pollutants to produce organic radical intermediates[159, 171]. These species undergo coupling or chain-growth reactions within the confined carbon interface, ultimately yielding polymeric products[90, 170]. Mechanistically, carbon-based catalysts and metal-based catalysts exhibit fundamentally different activation modes. Two major reactive pathways are generally involved: (i) long-range electron migration mediated by the three-dimensional conductive network (electron shuttling), and (ii) localized electron transfer governed by interfacial coupling effects (adjacent transfer)[90]. For carbon materials with extended π-conjugated structures, the presence of continuous electron-transport pathways renders long-range electron shuttling the predominant route, while local interfacial transfer plays only a supplementary role. In contrast, the intrinsic low conductivity of metal oxides restricts electron movement to short-range, coordination-controlled interfacial exchange. This fundamental discrepancy in electronic transport properties results in oxidation kinetics in metal-based systems that are typically 1–2 orders of magnitude slower than those of graphitized carbon materials[90].

3.4. Singlet oxygen

Singlet oxygen ($^1O_2$), a representative non-radical reactive oxygen species, is widely generated across advanced oxidation technologies, including ozone-based catalysis, photochemical activation, and persulfate-driven systems[172-176]. Although its standard oxidation potential is relatively low (0.81 V_{NHE}), $^1O_2$ exhibits distinctive kinetic advantages —such as a microsecond-level lifetime (2-4 μs) and a stable steady-state concentration (10^{-14}-10^{-11} M)—which underpin its high selectivity and controllable reactivity within aqueous environments[177, 178]. Its extended diffusion range and persistent presence enable efficient and targeted oxidation of phenols, sulfonamides, and other electron-rich contaminants that frequently occur in natural waters[179, 180]. Compared with conventional radical-mediated AOPs, $^1O_2$-dominated systems display superior tolerance to common water matrix components, including inorganic ions and dissolved organic matter, thereby minimizing competitive scavenging effects[181, 182]. This resilience arises from its unique electronic excitation and reaction pathways, which avoid the non-selective attack characteristic of hydroxyl and sulfate radicals[8]. Consequently, $^1O_2$ offers a promising, matrix-resistant route for achieving selective oxidation and efficient pollutant removal in complex water environments[178, 183, 184].

$^1O_2$, an electronically excited state of molecular oxygen, is a key non-radical reactive oxygen species in AOPs. Its reactions with organic compounds generally proceed through three pathways: (1) electrophilic addition, in which $^1O_2$ adds to electron-rich sites such as unsaturated bonds or aromatic rings[185, 186]; (2) electron transfer, where electrons are transferred from pollutants to $^1O_2$, producing $O_2{\bullet}^-$ and related oxidative species[178, 187]; and (3) heteroatom addition, whereby $^1O_2$ forms peroxidic adducts with N-, S-, or P-containing functional groups[188]. Among these pathways, electron transfer dominates the $^1O_2$-induced polymerization process. Pollutants bearing electron-donating substituents (e.g., alkyl or hydroxyl groups) readily transfer electrons to $^1O_2$, generating $O_2{\bullet}^-$ while converting themselves into radical cations or phenoxy radicals, which subsequently initiate polymerization[178, 189, 190]. Wang *et al*. reported that in the degradation of Bisphenol AF (BPAF), $^1O_2$ first attacks its symmetric phenyl rings via single-electron transfer to form phenoxy radicals[8, 191]. Fukui function analysis further indicates that the meta-positions on the aromatic ring, characterized by high electron density, show the highest reactivity toward $^1O_2$, leading to the formation of reactive intermediates and their gradual transformation into polymeric products[184, 192, 193]. Throughout this process, electron transfer continuously generates radical precursors, driving chain-growth reactions and ultimately yielding structurally diverse polymers. Moreover, $^1O_2$ exhibits pronounced oxidative selectivity, reacting at markedly different rates with different classes of pollutants. For instance, phenolates and sulfonamides containing anilide structures are far more reactive toward $^1O_2$ than alkanes, alcohols, or unsubstituted aromatic compounds, which further influences their polymerization behavior in oxidative systems[178].

3.5. Direct oxidative transfer process

As a major water treatment strategy, AOPs rely on the controlled generation of ROS to oxidize pollutants, yet their broader application is challenged by high energy inputs and the recovery of metal catalysts[8, 16-19]. Improving both efficiency and sustainability remains a key research need[21, 194, 195]. Yu *et al*. recently proposed the direct oxidative transfer process (DOTP), a mechanism that removes pollutants using minimal oxidant without forming by-products[195]. Unlike conventional AOPs, DOTP is an interfacial, ROS-independent pathway: the oxidant acts only as an electron acceptor[196]. Pollutants and oxidants co-adsorb on the catalyst surface, become simultaneously activated, and undergo spontaneous two-electron oxidation, generating intermediates that polymerize and form stable deposits on the catalyst[23, 197, 198]. DOTP also shows a clear structure–activity relationship. Pollutants with 1-2 active hydrogens mainly form oligomers via C–C coupling,

while those with 3-4 active hydrogens produce high-molecular-weight polymers through continuous chain growth. This difference reflects the role of active hydrogen sites in radical generation and coupling pathways. [24, 195] Because DOTP operates through direct, non-destructive oxidation, it is compatible with various oxidants and low-cost catalysts. However, the research on oxidation polymerization mechanisms initiated by DOTP remains relatively underexplored. Consequently, this review presents a concise discussion of DOTP as an auxiliary pathway, aiming to offer a conceptual framework and serve as a reference for future investigative endeavors in this domain.

4. Strategies for oxidative polymerization *via* radical pathways

In radical-based oxidation systems, pollutant degradation usually has two competing pathways. These pathways are mineralization and polymerization (Table 3). Traditional radical treatments take mineralization as the main way. Polymerization is usually seen as a minor process. However, the polymerization pathway can be greatly improved. This is done by adjusting ROS levels, controlling pollutant concentration and redox potentials, and adding nanoscale confinement effects. These methods bring new ways to control radical reaction selectivity. They also give theoretical support for the development of resource-based pollutant conversion technologies.

4.1. Concentration-synergistic regulation

Both the concentrations of ROS and organic pollutants are key regulatory factors influencing the degradation pathways of pollutants[195, 200]. At high ROS concentrations, the strong oxidative power of ROS governs the deep oxidation of pollutants. In high-concentration ROS systems, the continuous generation of radicals such as •OH and $SO_4^{\bullet-}$ accelerates the cleavage of pollutant molecular bonds, promoting the further breakdown of degradation intermediates into inorganic products such as CO_2 and H_2O, thus significantly enhancing mineralization efficiency[201, 202]. In contrast, the concentration of the pollutant monomer influences the feasibility of the polymerization reaction pathway through molecular collision probabilities. In the oxidation-polymerization reaction of the same organic pollutant molecules, the concentration of pollutant monomers (mM) is significantly higher than the concentration of the target pollutant in the system (μM)[203-206]. A higher concentration of pollutant monomers increases the likelihood of collisions between organic radicals, leading to the formation of polymeric products through chain-growth reactions. When the pollutant concentration is low, the concentration of reaction intermediates decreases, hindering effective collisions between intermediates. Thus, it can be inferred that both high ROS concentrations and low pollutant concentrations are unfavorable for the polymerization reaction. The ratio of ROS to organic substrates influences whether the reaction tends to proceed toward mineralization or polymerization. Research has shown that when the ratio of pollutants to oxidants in the system is significantly high (i.e., [pollutant]/[oxidant] > 20), the system exhibits "weak oxidation" characteristics[147, 196]. Under these conditions, the oxidation degradation pathway of organic pollutants is suppressed, and instead, radical intermediates promote the formation of stable products through polymerization (Figure 3). Additionally, studies have indicated that in Fenton-based systems, high concentrations of organic substrates ($[monomer]_0$:$[H_2O_2]_0$ > 50) and sufficient OH initiators ($[H_2O_2]_0$:$[Fe^{2+}]_0 \approx 3:1$) are favorable for achieving maximum conversion of monomers into polymerized products[207].

In radical-based pathways, the modulation of ROS generation through energy field control has been established as an effective strategy for optimizing pollutant degradation pathways[26]. For example, in the PS system, when the concentration of organic pollutants is fixed, thermal field control can significantly influence the selectivity of the reaction pathway. When the temperature is within the range of 50-80°C, the relatively insufficient thermal activation efficiency limits ROS production, thus hindering the mineralization process of pollutants. During this temperature range, intermolecular polymerization reactions dominate, and the amount of polymerization products increases with rising temperature. Notably, when the temperature exceeds the critical value of 90°C, the mineralization pathway becomes the dominant mechanism, while the formation of polymerization products is significantly suppressed. This temperature-sensitive regulation pattern has been validated in the study by Li *et al*[49, 147]. Additionally, electrochemical control methods also demonstrate precise and controllable advantages. For instance, research by Liu's team in the electro-Fenton system has shown that fine adjustment of the current density can dynamically control the steady-state ROS concentration, thereby effectively regulating the pollutant degradation pathway[26]. This approach further confirms the impact of varying oxidant-to-pollutant ratios on the degradation pathway, providing a more refined strategy for pollutant degradation. In the future, controlling these ratios could enable the radical pathway to favor oxidative polymerization, offering a more precise regulatory strategy for the resource utilization of pollutant degradation.

4.2. Oxidation-reduction potential

Review of current literature shows that under weak oxidation conditions (e.g., involving weak oxidants), organic pollutants are more likely to undergo polymerization reactions. Conversely, strong oxidative radicals (such as •OH and $SO_4^{\bullet-}$) mainly break down pollutant structures. They cause oxidative degradation instead of polymerization. The key factor that affects this difference is the redox potential[90, 208]. ROS usu-

Table 3. Key controlling factors for mineralization *vs.* polymerization in AOPs systems

Controlling Factors	Mineralization-dominated	Polymerization-dominated
Oxidation-reduction potential	High oxidation-reduction potential favors the initiation of mineralization pathways	Lower oxidation-reduction potential favors polymerization reactions
Oxidant type	Strong oxidants, such as •OH, $SO_4^{\bullet-}$	Mild oxidants, non-radical species like singlet oxygen ($^1O_2$)
The concentration ratio of ROS to organic pollutants.	The higher the concentration ratio, the easier the mineralization.	The lower the concentration ratio, the easier the polymerization.
pH range	Typically favors mineralization at lower pH	Polymerization generally occurs under neutral or slightly alkaline conditions

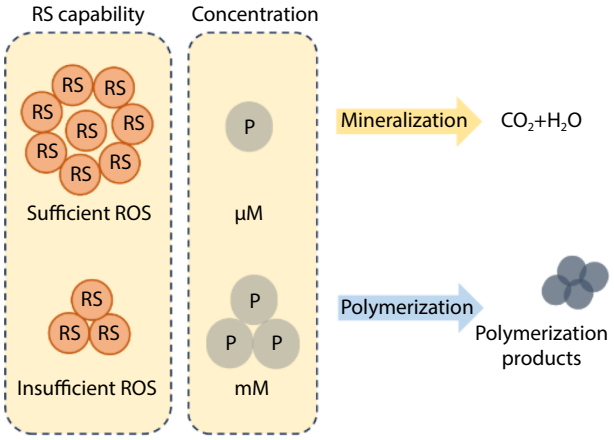

Fig. 3. Comparison of mineralization and oxidative polymerization induced by free radical pathways of organic pollutants and RS concentration.

ally show strong oxidation ability[18, 209]. Thermodynamic studies point out that for both oxidative polymerization and mineralization of pollutants, the first oxidation step of the monomer/pollutant (e.g., hydroxylation) is a non-spontaneous process ($\Delta G > 0$). It needs external energy from oxidants to push the reaction forward[210-214]. However, the later pathways of these two reaction types differ greatly. In oxidative polymerization, radical polymerization and chain growth after chain initiation are all thermodynamically spontaneous and exothermic steps. Conversely, mineralization needs continuous participation of highly oxidative (high redox potential) ROS species. They oxidize pollutants step by step into final products (e.g., CO_2 and H_2O). A strong oxidation environment must be kept the whole time[18, 209]. According to these mechanisms, oxidative polymerization can be started selectively with weak oxidants. This avoids structural damage to intermediates caused by excessive oxidation. For instance, in the UV-activated persulfate (UV/PDS) system. PDS decomposition produces highly oxidative $SO_4^{\bullet-}$ (E^0 = 2.5-3.1 V) and •OH (E^0 = 2.8 V). These reactive species interact with nitrite ions (NO_2^-). They form nitrosyl radicals ($^{\bullet}NO_2$, E^0 = 1.03 V) with a lower oxidation potential. This second type of radical has weaker oxidation ability. It stops mineralization paths and selectively helps form nitrosated polymeric products[215, 216]. This method of boosting oxidative polymerization through adjusting the oxidation environment provides a precise way to control pollutant degradation. It guides the process to polymerization instead of mineralization.

4.3. Nanoconfinement

Nanoconfinement describes a special phenomenon where reactants in the 1-100 nm space show different physical and chemical properties. These traits differ from macroscopic systems due to size effects, surface effects and quantum effects[217]. Its core working mechanism is clear. Reactions take place in nanopores, interfaces or micro-reaction chambers. The diffusion of radicals and reaction intermediates is greatly limited. This causes local concentration enrichment of substances[218, 219]. The chance of chain growth, coupling or condensation reactions rises greatly. It is much higher than that in bulk systems[218, 219]. In radical-mediated oxidation processes, nanoconfinement lowers non-selective attack from •OH, $SO_4^{\bullet-}$ and other high-activity radicals. It restrains excessive oxidation or mineralization of pollutants. It also extends the stay time of organic radical intermediates, raising their effective collision frequency and pushing forward the extension of polymer chains[220] (Figure 4). Graphene aerogel (GA) is a typical nanoconfinement material. Research results show a clear trend. The traditiona l(UiO-66-NH_2-(Zr/Fe)/GA + H_2O_2) system depends on constantly produced •OH radicals. These radicals realize step-by-step mineralization of pollutants. However, due to restricted radical diffusion and a single reaction pathway, the degradation speed stays at a low level. Adding GA to build a nanoconfinement system (UiO-66-NH_2-(Zr/Fe)/GA + H_2O_2) changes the situation. It increases degradation rates by nearly two orders of magnitude and significantly enhances reaction kinetics[147, 200, 221]. Concurrently, intermediate and product analysis shows another change. The reaction path turns from mineralization to oligomerization. Nanoconfinement plays a key role in this process. It realizes local enrichment of radical intermediates and raises their effective collision chance, thereby promoting thermodynamically preferred oligomerization pathways[200]. Thus, nanoconfinement is an effective method to strengthen radical oxidation polymerization. It helps raise polymerization efficiency and push forward pollutant resource conversion, showing wide material applicability and universal mechanism features.

5. Strategies for oxidative polymerization *via* non-radical pathways

In pollutant conversion research, non-radical reaction mechanisms serve as main pathways for oxidative polymerization. This method has clear advantages over traditional ways. It helps realize resource conversion of pollutants (Table 3). Multidimensional engineering controls can greatly lift reaction efficiency. These controls include electronic control (e.g., *d*-band cente), microstructure technologies (e.g., vacancy sites, interlayer structure), and composite support design (e.g., carbon-supported metals, metal-organic frameworks). These combined control methods effectively boost directional polymerization and conversion of organic matter by changing kinetic parameters of reaction paths. They provide a new route for the development of green chemical processes.

5.1. Electronically controlled

Metal-based catalysts are widely used in AOPs because of their high efficiency in removing pollutants in different systems. Among them, high-valent metal oxides perform well in non-radical pathways. Therefore, rational design of metal-based catalysts can effectively regulate the oxidative reaction pathway of

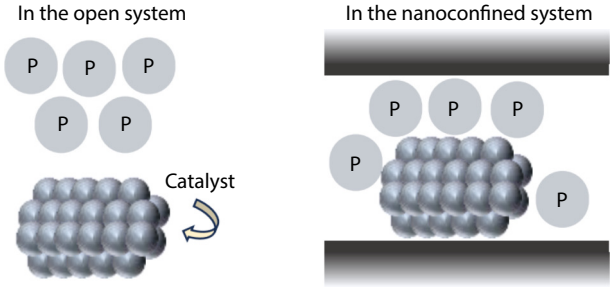

Fig. 4. Nanoconfined enrichment of contaminants to promote molecular aggregation strategies.

polymers and reduce carbon loss[222-224]. However, the formation of high-valent metal-oxygen species, such as Cu(III)-O and Fe(IV)=O, faces significant challenges due to the action of the 'oxygen wall', which limits their formation. Yu *et al*. developed an effective organic pollutant degradation strategy based on the regulation of metal *d*-band center(Figure 5b). Their research indicates that dynamic improvement of the electronic structure of high-valent metal oxide active sites can precisely control contaminated polymer processes[225-227]. The research team found that adjusting the *d*-band center of transition metal catalysts can significantly alter the redox characteristics of metal and oxygen types. Specifically, reducing the center of the *d*-band can improve the the electron capture efficiency of high-value metal oxides and promote the complete conversion of pollutants into polymer products. Experimental data shows that under the specified *d*-band center control conditions, the system achieved 100% conversion of pollutants into polymer products. For example, Fe(IV)=O with a *d*-band center exhibits the higher strong oxidation strength, but the polymer selectivity of phenol is only 44.9%. In contrast, Cu(III)-OH, Ni(IV)=O, and Co(IV)=O with lower *d*-band centers achieved almost 100% selectivity in polymer reactions[228](Figure 5a). Subsequent studies introduced the concept of high torque effect, which involves asymmetric joint activation with metals with different electronic activities to extract electrons from the *d*-orbitals of the target metal, thereby reducing the center of the *d*-band[228]. This modification improved the electronic structure and promoted the effective and sustainable production of high-value metal oxides in the later stage [228, 229]. In summary, by controlling the *d*-band center of metal based catalysts, their oxidation ability can be precisely adjusted, thereby enhancing polymer pathways, effectively removing organic pollutants, and reducing carbon emissions.

5.2. Microstructure regulation

Microstructure modulation plays a crucial role in determining the activity, selectivity, and stability of AOP catalysts. By customizing the configuration between defect structures, layers, and coordinated environments at the atomic level, electronic structures can be improved, the density of active sites can be increased, and the formation of interactive intermediates can be accelerated. Air oxygen engineering enhances surface reactions by redistributing charges and improving oxidation activation, while structural adjustments between layers provide structural elasticity to stabilize high-value intermediates and enhance non-radical oxidation. The following two sections summarize the latest developments in these two fine structure strategies and explain their key roles in improving catalytic oxidation efficiency and controlling contaminated polymer processes.

5.2.1. Oxygen vacancies (V_O)

Defect engineering is an effective method for enhancing catalyst activity, typically divided into internal and external defects, including metal vacancies (V_M), oxygen vacancies (V_O), and network vacancies (V_L)[230-233]. These defects disrupt the conventional network arrangement of the material, leading to the redistribution of local charges and thus improving the surface electronic properties of the material[234]. In AOPs, the oxygen vacancies (V_O) function is the key structure of catalyst defects. By changing the electronic structure, surface active sites, and mass transfer process of substances, V_O significantly improves the efficiency and selectivity of oxidation reactions[235-237]. The oxygen vacancies formed on the catalyst surface through defect engineering exhibit a stable absorption configuration, thereby increasing the density of active sites[207, 238](Figure 6). It also promotes binding interactions between catalysts and oxidizing molecules, improves electron accumulation and transfer, and facilitates electron transfer between catalysts and pollutants. By precisely controlling the concentration and distribution of oxygen vacancies within the catalyst, the efficiency and selectivity of polymer reactions can be significantly improved[145]. For example, in the study by Xie et al., manganese-based catalysts with varying oxygen vacancy contents were prepared by adjusting reaction conditions. After being activated by oxidation, these catalysts exhibit excellent pollutant removal efficiency. Experimental data shows that an increase in oxygen void concentration accelerates the chemical absorption of oxidation and promotes non root reaction processes. Specifically, the MnOx-180 catalyst exhibits the highest oxygen void content and dominant Mn^{4+} surface percentage, demonstrating optimal performance and removing over 90% of pollutants within 15 minutes[239]. In addition, the synergistic effect of oxygen vacancies and high-value metals creates a favorable environment for the conversion of pollutants into polymer products, reduc-

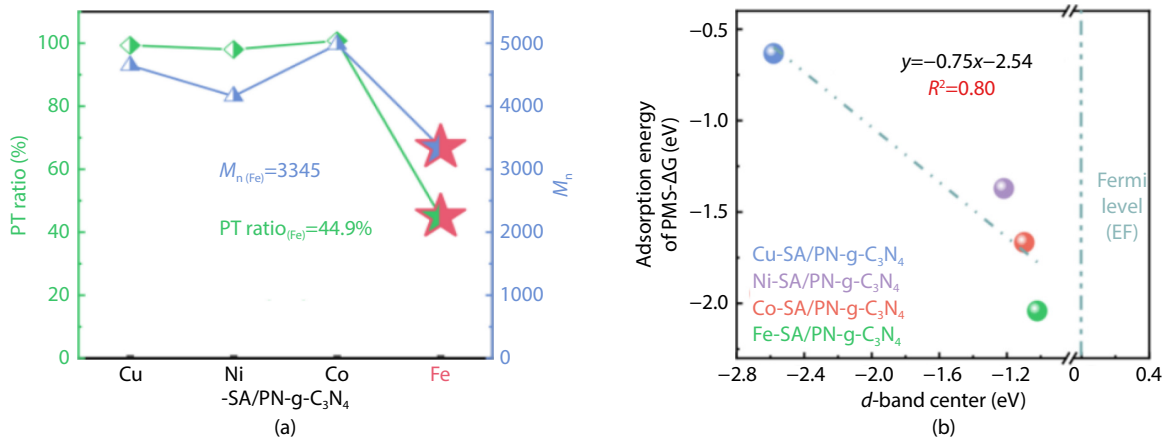

Fig. 5. (a) The PT ratios and Mn of the elution products in the four TM-SA/PN-gC_3N_4/PMS systems (PT: polymerization transfer; M_n: molecular weight; Reproduced with permission. [228] Copyright 2024, Springer nature. (b) Different metal *d*-bands center. Reproduced with permission. [228] Copyright 2024, Springer nature.

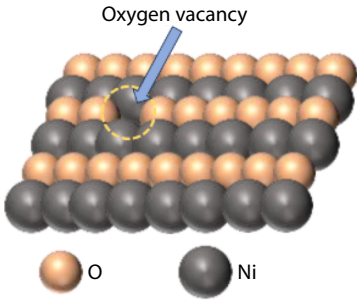

Fig. 6. Enhancing polymerization reaction efficiency by precisely controlling the concentration and distribution of oxygen vacancies within the catalyst.

ing the formation of harmful by-products and thus improving the overall efficiency of the reaction[240]. In summary, V_O greatly enhances catalytic and selective activity by altering the electronic properties of metal oxides and promoting the formation of active materials, providing a promising solution for the sustainable decomposition of organic pollutants.

5.2.2. Interlayer structure

Structural modulation of active centers is often a factor in regulating catalytic functionality[241, 242]. However, recent research on redox-active catalysts has largely focused on the reductive embedding and electronic regulation of electron-rich organic molecules within catalyst frameworks, while relatively neglecting how geometric and coordination-environment tuning of the intrinsic active sites governs reaction pathways and the formation of reactive intermediates[243-245]. Taking layered FeOCl as an example, its catalytic degradation of H_2O_2-driven pollutants mainly follows the traditional Fenton pathway. The FeO_4Cl_2 octahedral layers, stacked through Cl–Cl van der Waals interactions, endow FeOCl with outstanding H_2O_2 homolytic cleavage capability; the generated •OH exhibits one of the highest production rates among iron-based systems[10, 246-248]. Notably, Wang and co-workers constructed a novel K–FeOCl intercalation compound via K^+ insertion. The introduction of K^+ not only stabilizes high-spin Fe(II) active sites but, more importantly, induces a 0.1–0.2 Å elongation of the Fe–Cl bond during oxidation, thereby creating a responsive dynamic coordination environment (Figure 7). Such coordination flexibility significantly promotes the formation of Fe(IV)=O species and favors a two-electron transfer pathway, enabling highly efficient oxidative polymerization of organic pollutants. This work clearly demonstrates that flexible coordination environments play a crucial role in the generation of high-valent metal–oxo intermediates, offering a new structural strategy for tuning the intrinsic activity of catalysts[113]. A similar structure–activity relationship can be observed in cobalt-based systems. Under heterogeneous conditions, Co active centers often undergo irreversible decay from Co(IV)=O to Co(III) due to strong electronic repulsion with electron-rich oxygen species and the absence of interfacial confinement or steric regulation, ultimately leading to catalytic deactivation. Experimental evidence shows that constructing layered frameworks through Mg doping effectively suppresses this deactivation process: the modified interlayer environment mitigates the electronic relaxation tendencies of high-valent cobalt and stabilizes the evolution of Co(IV)=O intermediates, thereby markedly accelerating the kinetics of pollutant oxidative polymerization[249]. Collectively, regulating the interlayer structure, coordination flexibility, and electronic environment of catalysts can greatly enhance the generation of high-valent reactive species and accelerate non-radical oxidative polymerization pathways, thus advancing wastewater purification technologies toward higher efficiency and controllability. Structural modulation is therefore not only an essential component of active-center engineering but also a key strategy to promote non-radical oxidative polymerization, offering more systematic guidance for the future design of environmental catalytic materials.

5.3. Composite carrier design

In AOPs, carbon-supported metal and organic metal frameworks (MOFs) have become representative catalytic systems for effectively promoting non root oxidized polymers. Carbon-supported metals mainly improve catalytic performance through electronic interface pairing and defect engineering, while MOFs achieve path regulation through programmable coordination structures and locking effects. With the transi-

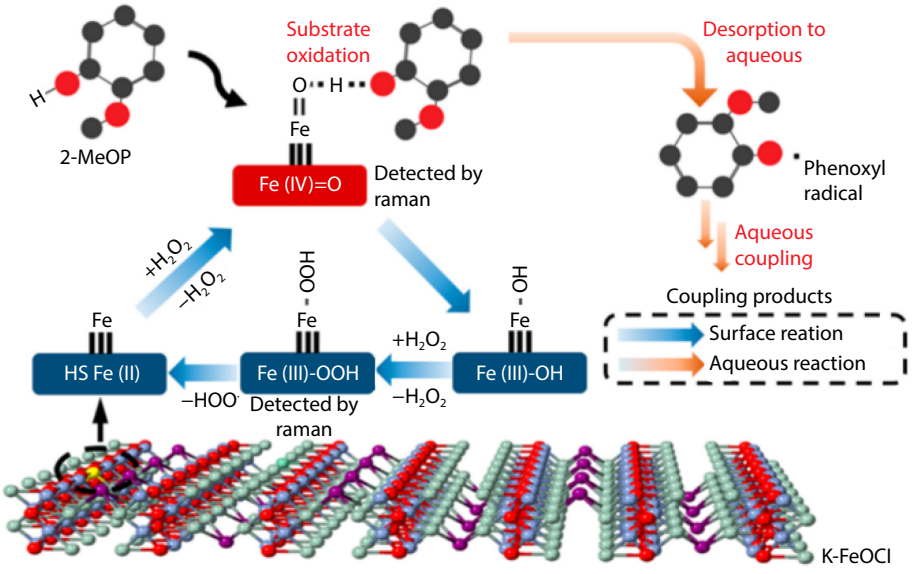

Fig. 7. Interlayer structure design promotes K-FeOCl-catalyzed oxidation polymerization of pollutants. Reproduced with permission[113]. Copyright 2022, Elsevier.

tion from radical decomposition to polymer modulation, these two systems demonstrate significant advantages in stabilizing high-value raw materials, promoting selective oxidation, and accelerating polymer movement. This section summarizes the latest advances in carbon supported metals and MOF-based catalysts, and emphasizes their mechanical role in achieving effective non-radical oxide polymers.

5.3.1. Carbon-Supported Metal

In AOPs, catalysts can be classified into different types based on carbon and minerals [250-252]. In recent years, the development of catalysts has evolved from a single physical method to a synergistic activation strategy that combines metal and carbon based catalysts[253]. Carbon materials have high defined surface area, excellent conductivity, and adjustable surface functional groups[39,166]. It can effectively disperse active metal components, prevent the aggregation of metal clusters, and improve the electronic structure of active metal sites[250,251]. The interaction between metal types and carbon carriers greatly regulates the coordinated environment and electron density of metals. This demonstrates the high value of mineral oxygen (such as M(IV)=O) and prevents its spontaneous decomposition, thereby promoting selective oxidation processes through non root pathways [250,251]. In addition, defect sites, non atomic doping agents (such as N, S, P), and π–π interactions on carbon support enhance the directional absorption and electron transfer efficiency of oxidation [54,169,170]. This helps active oxidation types participate in two electron transfer processes, promoting the gradual oxidation of organic pollutants and cross polymerization [235-237]. In addition, the possibility of regulating water/carbon substances in water increases the abundance of pollutants in the catalytic interface, thereby enhancing the movement of interface reactions [39,166]. At present, carbon supported metal catalysts exhibit significant structural and electronic advantages in non-radical oxide polymers, and are developing towards high efficiency, low carbon footprint, and intelligent applications. Research has shown that the loading of metals on carbon based materials affects their crystallization, but has little effect on the properties of surface functional groups. The mineral doping strategy can regulate the oxidation activity of carbon based catalysts[254]. For example, Zhi's team found through progressive copper doping experiments that introducing an appropriate amount of Cu can significantly improve the transportation efficiency of carbon based materials while detecting more active sites. In the PS activation system, the Cu-doped structure is activated through a non radical mechanism, extracting electrons from the aromatic benzothiafin ring (BT), generating free radical cationic intermediates, and complete polymer reactions. Among them, due to its rich active sites, the catalytic efficiency of the Cu-doped 6-Cu-UCN catalyst is significantly improved compared to the reference material, thereby accelerating the formation movement of the polymer [254] (Figure 8). Other studies have shown that the composite application of MXene nanosheets produces synergistic enhancement effects. When MXene conductors are combined with carbon materials carried by metals, the Ti(II)/Ti(III)/Ti(IV) and Co(II)/Co(III) redox pairs at the interface have highly efficient electron cycling capabilities, promoting the polymerization of bisphenol A (BPA). Experimental data shows that the dynamic stability of MXene composite material system has increased by 22.5 times, which has significant advantages over traditional non composite materials[255]. Therefore, carbon supported metal catalysts significantly enhance the oxidation of non root polymers through electronic interface pairing, stability of active species, and the influence of pollutant enrichment, providing an effective strategy for constructing highly selective and stable environmental catalyst systems.

5.3.2. MOFs

Organic metal frameworks (MOFs) are constructed through various interactions between metal nodes and organic bonds, including coordination bonds, hydrogen bonding networks, π–π accumulation, and van der Waals forces [256,257]. It provides advantages such as a very high specific surface area, adjustable pore size distribution, programmable chemical composition, and clearly designed metal active sites[256]. Traditional MOF stimulation systems typically rely on the reconfirmation cycle of mineral centers to generate roots that decompose pollutants. However, this mechanism often leads to car-

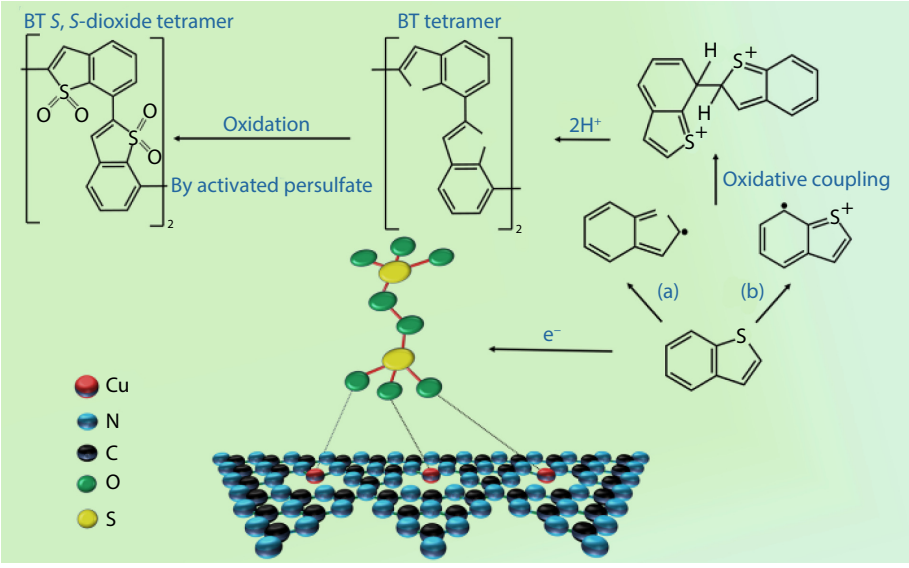

Fig. 8. Oxidative polymerization mechanism of BT mediated by persulfate and 6-Cu-UCN. Reproduced with permission[254]. Copyright 2023, American Chemical Society.

bon loss, degradation of activity sites, and decreased incentive efficiency. In recent years, new strategies have been proposed to overcome these limitations and achieve polymers targeting pollutants[257]. In terms of structural design and mechanism organization, the Zuo team has developed a heterogeneous core shell MOF@C composite system with MIL-101 (Fe) as the core and carbon graphite (TC) as the shell. In this system, $SO_4^{\bullet -}$ is generated for the first time in the kernel. Then, these roots diffuse to the interface of the carbon crust and are converted into $^1O_2$ through the C-O functional groups on the surface of the carbon layer. The resulting $^1O_2$ forms reactive intermediates by extracting hydrogen atoms, leading to pairing reactions and serial growth, thereby achieving polymer control of pollutants and stimulating the removal of hydrogen from pollutant particles. The experimental results indicate that the system's apparent rate constant value is 150.4 times that of the traditional homogeneous radical system, demonstrating significant motion advantages[258](Figure 9). In addition, the study also explored the composite system of MOF glass, utilizing the retention effect of glass to enrich oxidation and pollutants. This method can not only promote the formation of high-value metal oxygen, but also accelerate the transfer of interficial electrons by enhancing the electron tunneling effect, thereby increasing the push of targeted polymers towards pollutants[259]. These studies provide important mechanical insights into the non root polymer mechanisms driven by MOF stimulation systems: on the one hand, they can precisely regulate reactive oxygen species, and on the other hand, they enhance the nonconfinement effect. The research results not only demonstrate the potential of MOFs to enhance non-radical oxidized polymers, but also provide new perspectives and research guidance for the design and application of related catalysts.

6. Conclusions and Outlook

AOPs trigger oxidative polymerization via both radical and non-radical pathways, demonstrating significant potential in pollutant degradation, wastewater treatment, and the synthesis of functional materials. This review systematically summarizes the mechanistic characteristics of the two pathways and their related strategies to promote oxidative polymerization: (1) The radical pathway triggers the rapid oxidation and polymerization of organic matter through chain reaction, which has high reactivity but low selectivity, and is suitable for extensive degradation of complex systems. Based on the polymerization reaction of radicals, the ratio of reactive oxygen species to organic pollutants determines the pathway of mineralization and polymerization, mainly by regulating the concentration of ROS radicals, creating a "weak oxygen" environment, and strengthening the collision between intermediate molecules, so as to promote the reaction to polymerization. (2) The non-radical pathway (high-valent metal oxygen species, electron transfer, singlet oxygen, etc.) has high selectivity and anti-interference ability, which is especially suitable for the directional polymerization and resource recovery of target pollutants. The oxidative polymerization rate of non-radical pathways is enhanced by designing highly active catalysts such as *d*-band conditioning, defect engineering, metal-organic frameworks, interlaminar structures, and carbon-supported metal materials. Through the above analysis, it can be seen that in the degradation of catalytic organic pollutants, unlike the traditional oxidative degradation water treatment technology, the catalytic degradation mechanism of new organic pollutants starts from the essence of carbon migration, constructs the oxidative polymerization pathway of organic pollutants, and achieves the purification goal by regulating the molecular polymerization reaction of pollutants. The polymerization process can not only effectively degrade stubborn organic pollutants, but also recover organic carbon in water, reduce carbon emissions, and is expected to achieve carbon neutrality in wastewater treatment, which has broad prospects.

At present, research on non-radical oxidized polymers is still mainly limited to single substrate systems, and phenols and nitrites are commonly used as typical pollutants. However, in real wastewater, complex combinations of pollutants, multi-component reactions, fluctuations in ionic strength, pH changes, and intermediate stability can significantly affect polymer rate, product structure, and purity, thereby imposing significant limitations on practical engineering applications. Therefore, future research must go beyond the typical pillars of complex water systems and make further progress in catalytic structural engineering strategies. Interface engineering, defect adjustment, active site enrichment, and electronic structure design all require precise control of polymer pathways and intermediate development. On the other hand, the formation of high-value metal oxides, regulation of rotational states, and electron transport pathways can also determine the selectivity and molecular structure of products. Therefore, adjusting repeatability, electronic composition, and reaction environment is crucial for regulating polymer behavior and product

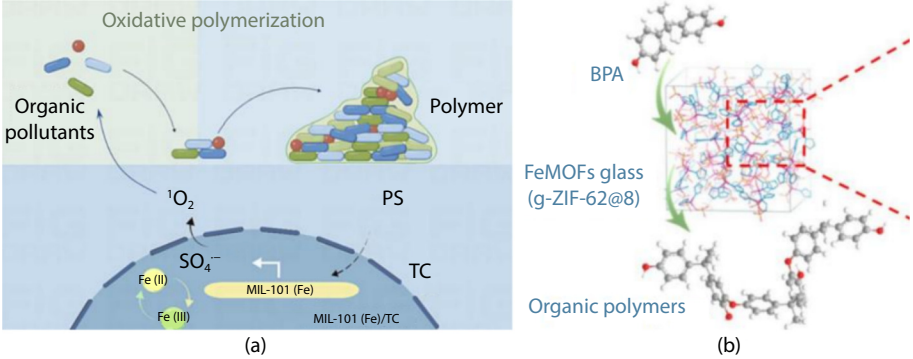

Fig. 9. (a) Possible oxidative polymerization interface reaction mechanism for bisphenol A removal in the MIL-101(Fe)/TC/PS system. Reproduced with permission[258]. Copyright 2023, Elsevier. (b) The confinement effect of MOF-glass promotes polymerization of organic pollutants. Reproduced with permission[259]. Copyright 2024, Elsevier.

quality (molecular weight, distribution, and purity), thereby promoting the conversion of polymers into value-added applications such as energy storage, carbon precursor, and catalyst reuse. Meanwhile, separating and recycling polymer products represents another bottleneck. Although polymers produced through filtration, centrifugation, or coagulation can be collected in a homogeneous system, they deposit on the catalyst surface, making the extraction process more difficult[171]. The current methods for extracting and distilling organic solvents have high energy consumption and lengthy processes. Therefore, there is an urgent need for low-energy, recyclable, and environmentally friendly separation technologies. In addition, it is necessary to assess the environmental risks of derived polymers, including migration behavior, bioaccumulation, and toxicity, to avoid the generation of secondary pollutants similar to microplastics.

Future research should focus on two main directions: (i) developing green and recyclable polymerization strategies to achieve long-term stability and reusability of catalysts; (ii) Combining on-site characterization with machine learning assisted mechanical analysis; Create reaction paths and catalyst fault maps for adaptive optimization. Recent studies have shown that providing a new technological pathway for reducing oxide consumption through a transition from fully aggressive mineralization to oxidative polymerization reduces carbon dioxide emissions and transforms pollutant resources. The advancement in catalyst design, interface chemistry, and mechanical understanding is expected to create a new paradigm for wastewater treatment that combines high catalytic efficiency with resource recovery and recycling.

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Conflicts of Interest

Jing Jin is currently employed by Yunnan Ningmao Environmental Technology Co., Ltd.. The authors declare no competing interests.

Ethical Approval

The English language of the article was improved with deepseek, developed by Hangzhou Deep Exploration Artificial Intelligence Basic Technology Research Co., Ltd.. After using the tool, the authors thoroughly reviewed and revised the material as needed and assume full responsibility for the final content of the publication.

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