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Review

Thermal catalysis under dark ambient conditions in environmental remediation: Fundamental principles, development, and challenges

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ABSTRACT

Thermal catalytic degradation of organic pollutants conducted in the dark at room temperature under atmospheric pressure without the need of external chemicals and energy sources has attracted a lot of attention over the last two decades. It provides unparalleled advantages over other advanced oxidation processes (AOPs) in treating domestic and industrial contaminated wastewater from the viewpoint of energy/chemical conservation and ease of operation. Rich knowledge has been accumulated in terms of the synthesis and application of thermal catalysts though controversies remain regarding their underlying mechanisms. This review sheds light on the proposed thermo-catalysis mechanism for the first time and presents the development of thermal catalysts under dark ambient conditions with a focus on catalyst materials, catalytic activity, and mechanism. The present review aims to provide mechanistic insights into the rational design of novel and efficient catalysts, and their underlying mechanisms as well as the emerging challenges and perspectives in thermo-catalysis under dark ambient conditions used for the practical and efficient treatment of contaminated wastewater.

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1. Introduction

Rapid industrialization and the ever-growing population worldwide have resulted in the increasing consumption of organic compounds in our society. The disposal of emerging organic contaminants (EOCs) such as pharmaceuticals, industrial chemicals, pesticides, surfactants, food additives, personal care products, and endocrine disrupting compounds from domestic and industrial wastewaters to an aquatic environment poses a great threat to wildlife, ecosystems, and human health [1,2].

Severe public concern has been raised on numerous water-related issues, such as water eutrophication, deteriorated water transparency [3], toxin enrichment, and aquatic photosynthesis disruption [4]. Strict policies have been implemented to impose restrictions on discharge limits regarding EOCs containing wastewater and legislate hefty penalties for non-compliance.

Apart from pollution source control, a range of diverse approaches have been developed to minimize the hazards of discharged organic pollutants, including (1) advanced oxidation

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processes (AOPs), (2) physical methods, and (3) biological treatment. Physical methods are generally considered ineffective in treating EOCs contaminated wastewater since they only transfer water contaminants downstream without achieving the degradation of the target pollutants, and tend to suffer from secondary pollution and regeneration issues. Biological treatment of wastewater requires the use of microorganisms or enzymes under harsh operation conditions (e.g., pH and temperature), and has poor applicability due to the sensitivity of organisms to the complex physicochemical environment of the various waterbodies treated [5]. Besides, it is generally not effective for synthetic dyes with recalcitrant nature [6,7]. AOPs utilize highly reactive species (ROS) generated in-situ via photocatalysis, electrochemistry, the Fenton reaction, or sulfate radical-based AOPs for the destruction of organic pollutants. The in-situ generated ROS (e.g., $\text{OH}^\bullet$, $\text{O}_2^{\bullet-}$, $\text{HO}_2^{\bullet-}$, and $\text{SO}_4^{\bullet-}$) can achieve the mineralization of most refractory pollutants into non-toxic/less toxic products (e.g., H_2O , CO_2 , and salts) in aqueous systems.

Interestingly, thermo-catalytic degradation of organic pollutants under dark ambient conditions has been widely reported with the aid of catalysts without additional energy input or chemical additives. For the sake of simplification, this type of reaction is referred to as thermal catalysis under dark ambient conditions in this review. Thermal catalysis under dark ambient conditions belongs to AOPs and demonstrates advantages over other AOPs in terms of energy/chemical saving and ease of operation through the use of irradiation, electricity, H_2O_2 , ozone, and sulphate. Hence, it provides huge potential in the practical treatment of organics-containing wastewater, particularly in problematic locations such as underground and in soil, where other AOPs are strictly limited.

Driven by the economic competitiveness and feasible operation of thermal catalysis under ambient conditions in environmental remediation, researchers have shown tremendous interest in this area and a wide range of innovative new materials have been reported as thermal catalysts for the degradation of organic pollutants under dark ambient conditions. It is well known that the primary task of the catalytic degradation of organic pollutants is to search for novel catalysts that exhibit high catalytic activity, super durability, and outstanding mineralization ability. Many research endeavors have been devoted to developing novel thermal catalysts in regard to their rational design and synthesis for use in the thermo-catalytic degradation of different organic pollutants in different systems.

It should be noted that although several catalysts have been reported to possess thermal catalysis under ambient conditions, fundamental insights into their underlying mechanisms, how and what ROS are involved, and the interplay among solvent/catalyst/pollutant/intermediates remain limited and sometimes controversial due to the lack of convincing experimental support and advanced characterization techniques. For example, energy-band engineering of catalysts has been widely accepted and adopted in photocatalysis to illustrate the transfer and recombination of photoexcited charge carriers (electrons and holes) and the generation pathway of ROS during the degradation of organic pollutants. However, no consensus has

been reached in thermal catalysis under ambient conditions regarding how electrons and holes are excited in the dark at room temperature without external irradiation (light, ultrasound, and microwave). In addition, knowledge on how the structure (e.g., crystalline phase, particle size, morphology, and exposed facets) and composition (e.g., active sites/phases) determine the thermal catalytic activity and stability under dark ambient conditions is still lacking. Furthermore, the roles of co-catalysts in enhancing thermal catalysis under ambient conditions for the degradation of organic pollutants are still ambiguous though it is generally believed that co-catalysts play a significant role in the catalytic process. All of the above factors warrant further research in order to gain fundamental insights on the factors affecting thermal catalysis under dark ambient conditions and to establish theoretical guidance for the rational design of novel, efficient, and robust thermal catalysts.

To our knowledge, no review article has been published to date regarding thermal catalysis under dark ambient conditions in water remediation. This critical review will clarify four thermal catalysis mechanisms under dark ambient conditions for the first time and highlight the recent advances in the degradation of organic pollutants under dark ambient conditions using thermal catalysts in regard to the catalyst type and activity. In addition, the intrinsic active species and nature of the catalysts involved in thermal catalysis under dark ambient conditions are identified and discussed. Besides, particular attention will be given to the controversial methodologies used for ROS identification and the limitations of thermal catalysis under dark ambient conditions in environmental remediation. The reactions occurring on the surface during the reaction pathway are illustrated in thermal catalysis under dark ambient conditions. The last section of the article provides critical comments on the future research direction for new advances and applications of thermal catalysis under dark ambient conditions in environmental remediation.

2. Thermal catalysis mechanisms under dark ambient conditions

Similar to classical heterogeneous catalysis, a thermal catalysis process under dark ambient conditions can be divided into the following five interactive steps [8]:

Reactant transfer from the fluid phase to the catalyst surface (Step 1).

Reactant adsorption onto the catalyst surface (Step 2).

Catalytic reactions occurring in the adsorbed phase (Step 3).

Products desorption from the catalytic surface (Step 4).

Transfer of the products from the interface region into the bulk solution (Step 5).

These five process determine the catalytic performance, reaction pathways and products. Various factors contribute to this process, such as pH, solvent chemistry, surface properties of the heterogeneous catalyst, and nature of the target reactants. Several excellent reviews have been published regarding the important parameters that affect heterogeneous reactions [9–14]. Although they are for photocatalysis, they still hold true for thermal catalysis under dark ambient conditions because

both are essentially heterogeneous catalysis.

Currently, there is no consensus regarding the thermal catalysis mechanism under dark ambient conditions, although several papers in this area have been published. The thermal catalysis mechanism under dark ambient conditions can be grouped into four categories based on the literature: (1) Surface electron-transfer mechanism, (2) hopping conduction model mechanism, (3) Mars-van Krevelen mechanism, and (4) free radical chain autoxidation mechanism. For all these mechanisms, the adsorption of organic pollutants is regarded as very important to allow fast and efficient catalytic reactions to occur (Eq. (1)).

2.1. Surface electron-transfer (SET) mechanism

In the SET mechanism (illustrated in Fig. 1), after the adsorption of organic contaminants onto the catalyst surface, electron injection from the pollutants to the catalyst via the conduction band or surface redox pair of the catalyst initiates the reaction with the concomitant generation of trapped electrons (catalyst (e^-)) and a semi-oxidized radical cation (Org.^+) (Eq. (2)). During this electron transfer process, the catalyst serves as an electron conductor. Trapped electrons will be consumed by adsorbed oxygen to yield anionic superoxide radicals ($\text{O}_2^{\cdot-}$) (Eq. (3)), which are protonated to form hydroperoxyl radicals ($\text{HO}_2^{\cdot}$) (Eq. (4)) and subsequently, H_2O_2 (Eq. (5)). The H_2O_2 formed further dissociates into hydroxyl radicals ($\text{OH}^{\cdot}$) (Eq. (6)). Singlet oxygen can be also generated via radical interactions (Eqs. (7)–(9)). Thus, the ROS are responsible for the degradation of organic pollutants and/or its semi-oxidized radical cation counterpart (Eq. (10)). In short, the catalyst for the SET mechanism acts as an electronic tunnel to facilitate electron transfer from the adsorbed contaminants to adsorbed oxygen via interactions between the active sites in the catalyst and contaminants, generating ROS for the degradation process.

The SET mechanism is prevalent in thermal catalysis under dark ambient conditions. Understanding how the charge transfer between the catalysts and reactants and what/how ROS are

Fig. 1. A schematic illustration of the surface electron-transfer mechanism for organic pollutant degradation under dark ambient conditions.

generated under dark ambient conditions is vital toward unravelling the thermal catalysis process. In addition, the band alignment of the catalyst and LUMO/HOMO in the organic pollutants should play a vital role in determining whether or not thermal catalysis under dark ambient conditions occurs, which is similar with the concept in photocatalysis. Further research will provide mechanistic insights into the auto-degradation process without external stimuli.

2.2. Hopping conduction (HC) mechanism

For the HC mechanism, when the energy received by the catalyst equals or exceeds the band gap energy of the catalyst, electrons in the valence band (VB) are excited into the conduction band (CB), leaving positive holes behind in the VB (Fig. 2). Highly oxidative holes can directly oxidize H_2O into hydroxyl radicals (Eq. (12)). Meanwhile, electrons can be trapped by adsorbed oxygen forming a series of ROS (Eq. (3)–(9)). The resultant ROS attack organic molecules to achieve thermo-catalytic degradation. Part of the excited electrons recombine with holes to dissipate the energy in a radiative or non-radiative manner (Eq. (13)).

2.3. Mars-van Krevelen (MVK) mechanism

There are two steps involved in the MVK mechanism. The first step is pollutant oxidation by the lattice oxygen in the catalyst, resulting in the generation of a partially reduced catalyst. Subsequently, the reduced catalyst is re-oxidized by O_2 (Fig. 3). It has been reported that lattice oxygen inside the catalyst can be activated to form active oxygen and an oxygen vacancy via the accompanied reduction of the active phases (high valence metals) in the catalyst [14], which triggers the consecutive formation of ROS (e.g., ${}^1\text{O}_2$, $\text{O}_2^{\cdot-}$, and $\text{OH}^{\cdot}$) for the degradation process [15–18]. Oxygen transfer between the catalyst and pollutant is believed to be the rate-determining step. In terms of the stability of the catalyst, re-oxidation of the reduced catalyst is vital in the MVK mechanism. Reduction induced oxygen vacancies in the catalyst can be filled by chemisorbed oxygen

Fig. 2. A schematic illustration of the hopping conduction mechanism in the thermo-catalytic degradation of organic pollutants.

Fig. 3. A schematic illustration of the Mars-van Krevelen mechanism in the thermo-catalytic degradation of organic pollutants.

via withdrawing electrons from any available donors [19].

2.4. Free radical chain autoxidation (FRCAO) process

In the FRCAO process, organic compounds (RH) become radical species ($R^\bullet$) via the reaction between RH and the catalyst (Cat.) (Eq. (14)) with the concurrent formation of the reduced catalyst (Cat_{Red}) (Fig. 4). The catalyst can be re-oxidized by adsorbed O_2 with the generation of $O_2^{\bullet-}$ (Eq. (15)), which will undergo further reaction to give $OH^\bullet$ (Eq. (4)–(6)). It is worth mentioning that $R^\bullet$ can also be produced via hydrogen abstraction of RH by $OH^\bullet$ (Eq. (16)). The addition of O_2 in $R^\bullet$ gives the corresponding peroxy radical ($ROO^\bullet$) as a chain carrier (Eq. (17)), which can abstract a hydrogen atom from RH to yield $R^\bullet$ and $ROOH$ (Eq. (18)). Alternatively, two $ROO^\bullet$ radicals may combine to give $ROO-ROO$ very quickly (Eq. (19)).

As discussed, distinct degradation mechanisms have been proposed to rationalize the thermal catalytic degradation of organic pollutants under dark ambient conditions. Efforts to probe the fundamental physicochemical processes in heterogeneous catalysis are of particular importance. For example, efforts should be dedicated to investigating the intrinsic properties of catalysts (e.g., electronic structures and surface states) and organic targets (e.g., HOMO and LUMO) to unravel the interactions between catalysts and substrates. The ROS involved should be determined using advanced in-situ techniques and their fate probed to provide insight toward elucidating the thermal catalytic degradation process of organic pollutants under dark ambient conditions [20].

It should be pointed out that catalytic wet air oxidation (CWAO) is not listed as an independent thermal catalysis mechanism in this section because all of the aforementioned mechanisms can be referred as CWAO that occurs under dark ambient conditions.

3. Catalyst materials

Approaches toward designing optimal heterogeneous catalysts rely on structure-function relationships between the active site characteristics and performance [21]. Variations in the catalysts in terms of their composition, active sites, surface structures, morphology, crystal structures, defects, and particle sizes have often been exploited to establish the structure-function relationships in thermal catalysis under ambient conditions. A summary of the dark ambient catalysts reported to date is listed below, focusing on the materials, catalytic activity, and underlying mechanism, based on the material classification of mixed metal oxides (including perovskites and others), single metal oxide/salt, doped metal oxides, hybrids, and hydrates.

3.1. Mixed metal oxides

Mixed metal oxides are complex oxides, which contain two or more metallic ions in various proportions. Their physicochemical features can be tailored at will and have wide applications in industrial catalysis [22]. To date, there have been a number of reports focusing on the synthesis and applications of mixed metal oxides used for wastewater treatment under dark ambient conditions, with perovskites being the most widely studied materials due to their unique physicochemical characteristics.

Perovskites are ceramic-type mixed metal oxide materials with the general formula ABO_3 (Fig. 5). Larger A-site cations (alkaline earth or rare earth metals) are located on the corners of the lattice and have 12-fold coordination with O. The smaller B-site cations (transition metal) reside in corner-sharing octahedral of the O anions [23]. The A/B site cation(s) can be replaced by 90% of the metal elements in the periodic table in the crystal structure without destroying the matrix structure [24]. This allows the thorough investigation of the structure-function relationships by doping foreign cations with different oxidation states or ionic radius. Due to the flexible electronic structure of the perovskite oxide family, their versatility for catalytic reactions relevant to the abatement of organic pollutants can be expected [25]. This is because the physicochemical properties (e.g., particle size, shape, morphology, lattice distortion, defects,

Fig. 4. A schematic illustration of free radical chain autoxidation of organic pollutants under dark ambient conditions without adding external oxidants or extra energy input.

Fig. 5. The ideal cubic perovskite structure for ABO_3 (light green ball represents the A atoms, Red ball for B atoms; and gold ball for O atoms).

and electronic properties) of perovskites will vary upon A/B site doping, thus opening experimental and computational opportunities to expand the composition and chemical reaction space for diverse perovskite-based engineered materials of interest using careful material design [26–32].

Recently, many reports have demonstrated the catalytic role of perovskites for organic pollutant degradation under dark ambient conditions without adding external chemicals and extra energy. Chen et al. [33] reported the thermo-catalytic degradation of orange II by $Ca_xSr_{1-x}CuO_3$ synthesized via a sol-gel chemistry method without adding any external chemicals. Fast kinetics were achieved with 80% OII (50 mg L^{-1}) removal in 10 min with excellent cycling performance (Fig. 6). The variation of Ca and Sr in the A site displays catalytic activity

though a higher Ca content enhanced OII degradation due to the systematic pH effect. The same group substituted Cu with Co and prepared a series of Co-based perovskites ($M_{0.5}Sr_{0.5}CoO_3$, $M = \text{Ba, Ca, and Mg}$) that also demonstrated a thermo-catalytic degradation capability for OII [34] though manifesting much less catalytic ability (80% in 4 h) when compared with $Ca_xSr_{1-x}CuO_3$ (Fig. 7). Besides, different A-site cations delivered diverse catalytic behavior in terms of the catalytic activity, degradation kinetics, degradation products, and cycling performance. Notably, OII degradation in the above two reports occurred via a SET mechanism initiated by azo bond ($-\text{N}=\text{N}-$) cleavage upon contact with the active catalyst, followed by the subsequent generation of ROS for further reaction.

Nickel has been widely used as a B-site cation in perovskite catalysts for the thermal catalytic degradation of organic pollutants under dark ambient conditions. It has been reported that $\text{LaNiO}_{3-\delta}$ (1.5 g L^{-1}) can achieve 94.3% degradation of methyl orange (MO) (5 mg L^{-1}) after 4 h under dark ambient conditions without any chemical stimulants and additional energy input [35]. The catalytic activity stems from lanthanum carbonate and the partial oxidation of nickel. However, the degradation mechanism is still unclear. Li et al. [36] prepared lanthanum nickel oxide (La_2NiO_4), which was used as a heterogeneous catalyst to degrade 4-chlorophenol in the dark. The degradation is initiated by the ionization of 4-chlorophenol into anions, which donate electrons to La_2NiO_4 . The donated electrons in La_2NiO_4 react with dissolved O_2 to produce highly re-

Fig. 6. (a) The effect of Ca and Sr cation concentration in the A-site of $Ca_xSr_{1-x}CuO_{3-\delta}$ for OII degradation. (b) The cycling stability of $Ca_xSr_{1-x}CuO_{3-\delta}$ ($x = 0.75$) [33].

Fig. 7. Normalized OII concentration (a), OII degradation kinetics (b), and cycling performance (c) of $MSrCoO$ ($M = \text{Ba, Ca, and Mg}$) [34].

Fig. 8. (a) The effect of the stirring rate on the catalytic activity of $\text{La}_4\text{Ni}_3\text{O}_{10}$ and (b) UV-vis spectra variation of MO over $\text{La}_4\text{Ni}_3\text{O}_{10}$ under stirring speed of 650 rpm [37]. Reprinted with permission from American Chemical Society.

active radical species ($\text{OH}^\bullet$) that are responsible for the mineralization of 4-chlorophenol. The results show that La_2NiO_4 also demonstrated catalytic activity towards phenol and MO under identical conditions. Layered perovskite $\text{La}_4\text{Ni}_3\text{O}_{10}$ was also reported for the thermo-catalytic degradation of MO [37]. Magnetic stirring can significantly enhance the dye degradation process. With a stirring speed of 650 rpm, ca. 100% MO (5 mg L^{-1}) was degraded after 3.5 h and 21% TOC was removed after 8.5 h (Fig. 8). Interestingly, they found $\text{La}_4\text{Ni}_3\text{O}_{10}$ possessed selective catalytic activity for degrading anionic azo dyes [MR, OG, and congo red (CR)] rather than cationic dyes Rhodamine B (RhB) and methyl blue (MB). The authors purged N_2/air , added Ag^+ , and measured the current-voltage curve and EIS spectra of $\text{La}_4\text{Ni}_3\text{O}_{10}$ to draw the conclusion that electron migration from MO to the catalyst initiated the degradation reaction, followed by the reaction between the donated electrons and dissolved O_2 to form the ROS responsible for MO degradation.

Very recently, Palas et al. [38] reported the CWAO of reactive black 5 (100 mg L^{-1}) with the aid of air and a LaNiO_3 perovskite catalyst (1 g L^{-1}) at 50 °C, atmospheric pressure, and pH = 3. It was found that 65.4% degradation and 89.6% decolorization were achieved in 2 h. The destruction of nitrogen to nitrogen double bonds initiated the decolorization with the for-

mation of aromatic intermediates due to the smaller enthalpy of the $-\text{N}=\text{N}-$ bonds than that of the $-\text{C}=\text{C}-$ and $-\text{C}-\text{H}$ bonds [39].

Iron is another widely investigated B-site cation used in the development of perovskite-type catalysts. By combining high temperature and high-energy ball milling processes, Liw et al. [40] prepared a SrFeO_3 perovskite, which was used for the thermal catalytic degradation of bisphenol A (BPA) and acid orange 8 (AO8) under dark ambient conditions. The complete degradation of BPA was achieved and 83% mineralized in one day, while fast discoloration of AO8 was achieved in 1 h, followed by the complete breakdown into primary intermediates and aliphatic acids in 24 h over the SrFeO_3 catalyst (Fig. 9). The surface adsorption of these anionic contaminants on positively charged SrFeO_3 contributed to the high degradation activity. $\text{O}_2^\bullet$ generated via the interplay of adsorbed oxygen and oxygen vacancies in the catalyst was reported to induce the observed thermal catalytic degradation of AO8 and BPA in the dark under ambient conditions.

The doping of Ce for Sr in SrFeO_3 resulted in $\text{Sr}_{0.85}\text{Ce}_{0.15}\text{FeO}_{3-\delta}$ which demonstrated good catalytic reactivity for OII decomposition at mild temperature (55–80 °C) in the dark without external chemicals [41]. Thermal-induced ROS

Fig. 9. (a) The degradation and TOC removal of BPA. (b) UV-vis spectra of the AO8 solution treated with SrFeO_3 . Inset: The UV-vis spectrum of 2-naphthol [40].

Fig. 10. The degradation of an OII solution over SrFeO at various temperatures [41].

(OH• and $^{10}\text{O}_2$) identified using the EPR spin-trapping technique achieved 95% degradation of OII (10 mg L^{-1}) in 6 h at 80°C (Fig. 10). Significant catalytic selectivity is observed for OII rather than RhB.

Significant catalytic selectivity is observed for OII rather than RhB. Su et al. [42] substituted Ti^{4+} with Mn^{4+} in SrTiO_3 and found Mn^{4+} in $\text{SrTi}_{1-x}\text{Mn}_x\text{O}_3$ was active for RhB degradation under dark ambient conditions. Approximately 50% RhB (10^{-5} M) degradation was achieved over $\text{SrTi}_{0.95}\text{Mn}_{0.05}\text{O}_3$ (1 g L^{-1}) after 4 h. The degradation of RhB in the dark was due to the thermal oxidative ability of Mn^{4+} via the irreversible partial reduction to Mn^{3+} encountered after the reaction.

In conclusion, foreign element doping or substitution strategy have been widely employed to advance perovskite materials as thermal catalysts under dark ambient conditions. The intrinsic catalytic properties of perovskite materials can be modified by partial replacement of the A/B-site metal with ions of different valence and ionic radius due to the varied oxidation state and resulting structural defects (anionic or cationic vacancies) [43,44]. It is widely accepted that B-site cations are catalytically active sites since the conduction and valence bands of the catalysts primarily consist of B_d and O_p orbitals, respectively [45]. However, as A-site ions can modify the structural and redox features of perovskites, one can expect the catalytic behavior of perovskite-type catalysts must be influenced by A-site cations. This is because larger A-site atoms contribute to stabilize the multiple valence states of the B-site cations and the structural framework [46], which further benefits the electrons of ABO_3 to be more active and excited easily once exposed to external stimuli [47]. Therefore, the relationships between catalytic activity and structure regarding the A/B-site cations in perovskites opens significant research opportunities and is of great importance in advancing perovskite-type thermal catalysts in environmental remediation under dark ambient conditions.

There are also other kinds of mixed metal oxides besides perovskites. A good example is CeGeO_4 , prepared via a solvothermal method [48], which can completely degrade RhB (3 mg L^{-1}) in 10 h with ca. 30% TOC removal and MB (6 mg L^{-1}) in

~24 h with 30% TOC removal under dark ambient conditions. However, no degradation mechanism was proposed in this study.

MoZnAlO has been widely investigated as a thermal catalyst for degrading organic pollutants under dark ambient conditions [49–51]. Xu et al. [49] synthesized a MoZnAlO catalyst using co-precipitation and impregnation methods, and evaluated its thermal catalytic ability for cationic red GTL at room temperature and atmospheric pressure. The catalyst can readily react with adsorbed $\text{O}_2/\text{H}_2\text{O}$ to produce $\text{OH}^\bullet$ and $^{10}\text{O}_2$ that are responsible for the degradation of cationic red GTL (Fig. 11). Under the optimal conditions (pH 4.0, initial dye concentration of 85 mg L^{-1} , and catalyst dosage of 2.72 g L^{-1}), 80.1% of cationic red GTL was decolorized with 50.9% TOC removed in 60 min. They further optimized the dark ambient catalytic activity of MoZnAlO for cationic red GTL degradation by varying the molar ratio of Zn/Al [50]. It was found that the catalytic activity and stability were correlated with the zeta potential, surface area, crystalline phases, Mo valences, and number of active adsorption sites available for the generation of $^{10}\text{O}_2$ and $\text{OH}^\bullet$. Meanwhile, Li et al. [51] investigated the effect of pH on the phase formation, structure, and catalytic activity of Mo-Zn-Al-O catalysts prepared via an impregnation process. The results show the pH value significantly influenced the speciation diagram of the Mo species and the catalytic activity. The highest catalytic activity occurred at pH = 7 with 94.6% decolorization and 86.7% TOC removal for cationic orchid X-BL in 10 min. Based on previous studies, the Xu's group [52] replaced Zn and Al in Mo-Zn-Al-O with Cu and Fe to give a Mo-Cu-Fe-O composite. The resultant material exhibited higher catalytic activity, reaching the complete decolorization of cationic red GTL (100 mg L^{-1}) in 1 h at a catalyst dosage of 1 g L^{-1} (Fig. 11). Moreover, the newly obtained catalyst also demonstrated excellent catalytic activity for crystal violet. It was found that the negative zeta potential, small crystalline size, the reducibility, and active O_2 adsorption sites of the catalyst play crucial roles in its catalytic activity.

Another mixed metal oxide $\text{Ni}_x\text{Fe}_y\text{Mn}_z\text{O}$ (1 g L^{-1}) synthesized via a co-precipitation method reached 83.8% degradation of

Fig. 11. Decolorization of wastewater containing cationic red GTL using a Mo-Cu-Fe-O catalyst with and without air aeration in the CWAQ process [52].

Fig. 12. A schematic illustration of the thermal catalysis mechanism of Mn-Si-Ca-Cu-Ni-O metal oxides [54].

MO (30 mg L⁻¹) in the dark at 50 °C in 40 h [53]. Hopping electrons and holes of Mn³⁺ to Mn⁴⁺ accounted for the observed thermo-catalytic activity. Luo et al. [54] synthesized Mn-Si-Ca-Cu-Ni mixed metal oxides via high temperature calcination. The resulting material (1 g L⁻¹) possessed thermal catalysis under dark ambient conditions and degraded 82.07% methylene blue (40 mg L⁻¹) in 30 h via a hopping conduction mechanism (Fig. 12).

Another Mn-containing quaternary metal oxide NiCoMnO₄ was prepared using a chemical co-precipitation method, which also showed thermo-catalytic ability for MB [55]. The thermo-catalytic activity was largely determined by the sintering temperature and reaction temperature. Using a calcination temperature of 700 °C and a reaction temperature of 50 °C, the removal efficiency of MB (10 mg L⁻¹) reached 75.9% after 10 h and 92.3% after 40 h with a 0.375 g L⁻¹ catalyst dosage. The degradation mechanism analysis suggests electrons were excited from the valence band to the conduction band upon heat excitation, leaving holes behind, with the aid of Mn³⁺/Mn⁴⁺ and Co²⁺/Co³⁺ redox pairs. The generated e⁻ and h⁺ undergo further reactions to achieve the thermo-catalytic degradation of MB.

Fe-doped Sr₂Bi₂O₅ prepared via a co-precipitation method showed thermal catalysis under dark ambient conditions for MB degradation [56]. The removal efficiency increased with the catalyst dosage and temperature, whereas it decreased with the initial MB concentration. It was found that 92.6% MB (20 mg L⁻¹) was degraded in 3 h at 50 °C with a catalyst dosage of 0.875 g L⁻¹. Heat energy with sufficient power excited Bi²⁺ to Bi³⁺, generating electrons and holes for the oxidative degradation of MB. Bi²⁺–O–Bi³⁺ functioned as a bridge for facile electron or hole transfer. Moreover, Fe³⁺ facilitated the separation of electrons and holes by serving as a hole and electron trap. TA-PL and radical quenching experiments demonstrated the crucial role of holes in the thermo-catalytic degradation of MB.

3.2. Single metal oxide/salt

The work by Ma and co-workers revealed the remarkable

catalytic activity and reusability of amorphous Ce(IO₃)₄ in degrading RhB, MO, and MB (10 mg L⁻¹ aqueous solution) in the absence of light irradiation or chemical additives at room temperature [57]. Ce(IO₃)₄ (1.5 g L⁻¹) can completely degrade RhB and MO in just 50 min, while ca. 58% MB in 8 h. Ce(IO₃)₄ demonstrated remarkably superior catalytic activity when compared to the above-mentioned CeGeO₄ catalyst under identical conditions. α-Fe₂O₃ synthesized via chemical precipitation was employed for the degradation of reactive brilliant blue X-BR (20 mg L⁻¹) under dark ambient conditions [58]. More than 95% was degraded in 8 min at a catalyst dosage of 0.1 g L⁻¹. The authors argued that positive holes and electrons would be generated in Fe₂O₃ upon excitation somehow, followed by the generation of ROS in a similar way to that observed in photocatalysis.

Zinc oxide (ZnO) is widely used as a photocatalyst for organic pollutant degradation. Surprisingly, Cai and co-workers found ZnO exhibited thermal catalytic activity as well for azo dye degradation under dark ambient conditions [59]. They found that exposed polar surfaces dramatically affected the catalytic activity and stability due to the distinct capability to absorb oxygen species (e.g., O⁻, O₂⁻, O₂, and OH⁻) and model pollutants. Systematic experiments were carried out to unravel the thermal catalytic process under ambient conditions for the ZnO samples. They concluded that dye degradation proceeded via electron transfer from the anionic dye molecules to the catalyst and subsequently to the electron acceptors (e.g., dissolved oxygen) (Fig. 13). Notably, the as-prepared catalyst was only active for anionic azo dyes (CR and MO) and not for cationic azo dyes (RhB and MB), similar to that previously reported for the La₄Ni₃O₁₀ catalyst [37].

Hierarchical structures in catalysts are generally beneficial to the catalysis process because they retard catalyst deactivation and enhance the catalytic process. By doping Mo into S/BiOCl, Zhang et al. [60] prepared hierarchical structured Mo-doped S/BiOCl using a facile one-step reflux method. The resulting materials possessed outstanding thermo-catalytic activity for methylene blue (30 mg L⁻¹) at 40 °C, reaching 96.5% degradation in 60 min. Both holes and radicals were involved in the thermo-catalytic degradation with holes playing

Fig. 13. The degradation mechanism of anionic azo dyes over ZnO under dark ambient conditions [59].

a major role.

3.3. Hybrids

Hybrid catalysts have been intensively researched in water treatment since they can potentially combine the benefits (e.g., high activity, adsorption ability, suitable redox property, and high surface area) of each single component, providing a promising strategy toward the design of highly effective catalysts for thermal catalysis under dark ambient conditions.

Li and co-workers [61] prepared CeO_2 and MoO_3 hybrids with varied amounts of CeO_2 and studied the dark ambient catalytic activity of the resultant materials for Safranin-T degradation. Under the optimal conditions (11.86 wt% Ce doping), 98% Safranin-T (0.3 g L^{-1}) was completely degraded into HCO_3^- and NO_3^- by CeO_2 - MoO_3 (1 g L^{-1}) within 20 min in the presence of air via $^1\text{O}_2$ and $\text{OH}^\bullet$ species. Moreover, the catalytic activity was maintained after ten cycles. The outstanding catalytic performance stems from the increased mobility of oxygen due to the oxygen transfer role of CeO_2 and benign interactions observed between MoO_3 and CeO_2 , as illustrated in Fig. 14.

Chen et al. [62] reported the synthesis of nominal $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{NiO}_3$ materials made up of a mixture of NiO , $\text{Ca}(\text{OH})_2$, and $\text{Sr}(\text{OH})_2 \cdot \text{H}_2\text{O}$ via a combined EDTA-citric acid complexation method. The as-synthesized materials exhibited extremely fast degradation kinetics towards OII under dark ambience. Approximately 97% of OII (20 mg L^{-1}) was discolored within 5 min. It was found that the catalytically active surface and irreversible oxidation of Ni^{2+} to Ni^{3+} after the reaction concurrently contribute to the effective degradation process. The catalyst surface was shown to be highly reactive for breaking the $-\text{N}=\text{N}-$ bonds present in OII molecules. Moreover, Ni^{2+} oxidation into Ni^{3+} further promoted the generation of reactive species, as shown in Fig. 15.

Combining the synergistic effect of the B-site cation Cu in $\text{Ca}_x\text{Sr}_{1-x}\text{CuO}$ [32] and Ni in CaSrNiO [62], Chen et al. [63] synthesized CaSrNiCuO metal oxides, which possessed both higher cycling performance than CaSrNiO and higher TOC removal ability than $\text{Ca}_x\text{Sr}_{1-x}\text{CuO}$ for OII degradation under identical experimental conditions.

The degradation of MO and RhB was studied using a CaSe -graphene nanocomposite in dark ambience [64]. The complete degradation of MO occurred and ca. 70% of RhB was removed in 60 min. The high degradation observed originated from the catalytic properties of CdSe and the excellent charge mobility of the graphene nanosheets. A $\text{Cu}_2(\text{OH})_3\text{NO}_3/\text{ZnO}$

Fig. 14. The proposed redox mechanism of CeO_2 - MoO_3 in the CWAO process [61].

Fig. 15. A schematic illustration of the OII degradation pathway over CSN: [I] Direct electron transfer and [II] nickel oxidation [62].

composite was synthesized via a combination of precipitation and hydrothermal treatment methods, which was used for the degradation of MO under dark ambient conditions without additional oxygen flow [65]. MO (500 mg L^{-1}) was dramatically degraded by the catalyst (3 g L^{-1}) with 99% color removal and 94% TOC removal in 20 min. Cu^{2+} serves as electron bridge between the MO molecules and electron acceptors (O_2) to induce the generation of reactive radicals for MO degradation.

Magnetic materials have intrinsic advantages over non-magnetic ones as heterogeneous catalysts due to the facile magnetic separation of the catalysts from the reaction system after the catalytic process. For this purpose, Yang and co-workers [66] synthesized magnetic imprinted N-doped $\text{P25}/\text{Fe}_3\text{O}_4$ -graphene oxide (MIGNT) and used it as a heterogeneous catalyst to degrade congo red (CR) under dark ambient conditions. The material had a high degradation efficiency for CR and could be recycled conveniently due to the magnetic properties of Fe_3O_4 . They postulated the degradation was initiated by electron transfer from $\gamma\text{-Fe}_2\text{O}_3$ into the valence band of P25, leaving holes behind. The presence of GO sheets and P25 accelerated the charge separation and facilitated the generation of reactive radicals for CR degradation, as illustrated in Fig. 16. However, although the degradation products were identified by HPLC-MS analysis, no direct evidence was given to prove the existence of the reactive radical species.

Similarly, Wei et al. [67] prepared a molecularly imprinted polymer (MIP)-coated magnetic TiO_2 nanocomposite ($\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2@\text{MIP}$) and used it for CR degradation under dark ambient conditions. The results showed that the catalyst could rapidly degrade CR and is easily recycled. The degradation mechanism resembled that of the MIGNT catalyst [66].

Xu et al. [68] prepared $\text{ZnAl-LDH}/\text{H}_3\text{PMo}_{12}\text{O}_{40}$ nanohybrids using a self-assembly method. The as-obtained catalyst (0.8 g L^{-1}) can decolorize 74.2% MO (100 mg L^{-1}) and remove 66.2% TOC in 10 min with high recycling performance. The authors proposed that the degradation was initiated by $\text{OH}^\bullet$ formation on ZnAl-LDH with PMo_{12} acting as an effective electron acceptor. Dissolved oxygen reacted with the trapped electrons in PMo_{12} to generate superoxide anion radicals. By employing a chemisorption-calcination cycle method, Jin et al. [69] prepared a Co_2O_3 - TiO_2 thermocatalyst, which degraded 80% 2-naphthol ($10 \mu\text{mol L}^{-1}$) in the dark at 323 K with a catalyst dosage of 2 g

Fig. 16. A schematic illustration of the CR degradation process on MIGNT [66].

L^{-1} . The electron transfer from 2-naphthol to the cobalt ions was the initiation step, followed by the generation of superoxide anion radicals, which are responsible for the degradation of 2-naphthol.

$\text{M}_2\text{Mo}_4\text{O}_{13}/\alpha\text{-MnO}_3$ ($\text{M} = \text{Li}, \text{Na}$ or K) hybrid catalysts were synthesized via a hydrothermal method and evaluated for cationic red GTL removal under ambient temperature and atmospheric pressure [70]. The catalytic activity increased with reaction temperature and there was an optimal calcination temperature observed during the materials synthesis. For materials calcined at 300°C and used at a reaction temperature at 20°C , ca. 100% discoloration and 93% TOC were removed by all three catalysts within 30 min in the presence of air. $\text{M}_2\text{Mo}_4\text{O}_{13}$ ($\text{M} = \text{Li}, \text{Na}$ or K) accelerates the formation of $\text{OH}^\bullet$ for the catalytic removal of the target dye pollutants. The same group prepared $\text{Na}_2\text{Mo}_4\text{O}_{13}/\alpha\text{-MoO}_3$ hybrid materials, which showed the highest ever activity for the thermo-catalytic degradation of cationic red GTL [71]. The presence of $\text{Na}_2\text{Mo}_4\text{O}_{13}$ increased the amount of O^{2-} ions in the oxygen deficient regions, which have higher mobility than lattice oxygen and enhance the generation of active $\text{OH}^\bullet$ for pollutant degradation. The higher pH value led to the higher degradation efficiency. Furthermore, the catalytic activity increased with calcination temperature up to 300°C , while it deteriorated with a further increase in temperature.

Platinum as a noble metal has often been used as an important co-catalyst in heterogeneous catalysis. For instance, Pt can facilitate the interfacial charge carrier separation in photocatalysis by serving as an electron sink, thereby enhancing the overall catalytic activity. Pt is also widely used in thermal catalysis under dark ambient conditions. Taking Pt- TiO_2 film as an example, the thermal catalytic degradation of formic acid was observed in the presence of air under dark ambient conditions [72]. The catalytic oxidation of formic acid was due to the high-oxidation activity and facile O_2 dissociation ability of nano-Pt on the Pt- TiO_2/ITO film. ca. 30% COD of formic acid (15 mmol L^{-1}) was removed by Pt- TiO_2/ITO in the dark in the presence of air in 30 min using 4.5 wt. Pt/ TiO_2 . Furthermore,

they concluded that the thermal catalytic activity of nano-Pt is highly sensitive to the preparation method used because Pt(TiO_2)/ITO did not show any thermal catalytic activity for formic acid.

Dvininov et al. [73] reported the feasible reduction of oxygen under dark ambient conditions using platinized semiconductor particles ($\text{Pt-HCa}_2\text{Nb}_3\text{O}_{10}$), which induced the complete demethylation of MO, which was confirmed by LC/MS. The observed room temperature air oxidation of MO may stem from the strong acidity due to the labile protons available for the partial and total oxidative reactions. Besides, the Brønsted acidity is combined with the presence of Ca^{2+} in addition to the d^0 center, which will enhance the donor power of the lattice oxide. However, solid evidence is lacking in regard the detailed degradation process.

Pt-based catalysts are optimal for HCHO decomposition at room temperature [74]. Zhou et al. [75] observed the enhancement in the catalytic activity of the Pt catalyst in the presence of alkali metal salts due to the presence of OH^- ions provided by the alkali metal salts. The OH^- ions contribute to the dual dehydrogenation of HCHO, which promotes the regeneration of Pt and the activation of O_2 (Fig. 17).

Similarly, Duan et al. [76] also reported the room temperature oxidation of formaldehyde into CO_2 and H_2O using tin oxide-supported platinum (Pt/ SnO_x) with hierarchical structures (Fig. 18). The as-prepared material showed enhanced Pt activity (87% HCHO removal in 1 h) when compared with Pt NPs supported on commercial SnO and ground SnO_x as well as high stability. The hierarchical pore structure not only facilitated the diffusion and adsorption of HCHO, but also dispersed the active Pt NPs uniformly on the SnO_x nanosheets.

The stability of thermal heterogeneous catalysts is as important as the activity when it comes to industrial applications. The same is found for Pt-based catalysts used for HCHO decomposition at room temperature. For example, the catalytic activity of the Pt- TiO_2 catalyst was decreased due to adsorbed halogen ions on the catalyst surface [77]. The adsorbed halogen ions form coordination bonds with the surface Pt atoms by

Fig. 17. Dual dehydrogenation of HCHO with two adjacent -OH groups on the Pt cluster [75].

transferring surplus electrons into the unoccupied 5d orbital of the Pt atoms, thereby inhibiting oxygen adsorption and the activation of the Pt NP surface (Fig. 19). Additionally, halogen ions with larger diameter exhibit a greater poisoning effect.

In addition to formaldehyde, Pt containing ZnO also demonstrated the green catalytic oxidation of benzyl alcohol in base-free aqueous medium at room temperature [78]. ZnO acts as a support and facilitates the adsorption of benzyl alcohol, which subsequently reacts with activated oxygen species on Pt with the production of benzaldehyde. Remarkably, Pt/ZnO showed a high conversion (94.1% in 10 h) of benzyl alcohol and almost 100% selectivity towards benzaldehyde using ambient air as the oxidant (Fig. 20). In addition, the introduction of Bi could further increase the activity by 3.5-fold.

Thermal catalysis can also be used for methanol oxidation using isolated surface vanadia (VO_4) species on SiO_2 [79]. The structurally identical surface VO_4 species can selectively oxidize methanol to formaldehyde, which is attributed to the different positions of the electronic states (HOMO/LUMO and valence/conduction band) on the electrochemical energy scale due to the quantum size effect.

Fig. 18. A schematic representation of the catalytic oxidation of HCHO on the Pt/ SnO_x catalyst [76].

3.4. Hydrates

Li et al. [80] obtained amorphous $\text{ZrHfO}_6 \cdot 4\text{H}_2\text{O}$ using a facile precipitation method and evaluated its thermal catalytic activi-

Fig. 19. A schematic representation of the catalytic oxidation of HCHO and halogen poisoning effect over the as-prepared samples [77].

Fig. 20. The time course of alcohol oxidation on Pt/ZnO under aqueous conditions at room temperature [78].

ty for RhB and MB degradation under dark ambient conditions. The complete degradation of RhB (3 mg L⁻¹) and MB (6 mg L⁻¹) was achieved within 16 h with 25%–30% TOC removal using a catalyst dosage of 1.5 g L⁻¹. ZrHfO₆·4H₂O demonstrated stable chemical properties and degradation activity after multiple runs. However, the underlying degradation pathway is still unclear. Another example of hydrates used as heterogeneous catalysts for pollutant removal is CeHfO₆·4H₂O, which showed thermal catalytic activity towards MB, RhB and MO under dark ambient conditions [81]. CeHfO₆·4H₂O can completely degrade these three dye pollutants in ca. 6 h and showed superior cycling performance and high chemical stability after cycling experiments. It was found that the I⁷⁺/I⁵⁺ and Ce⁴⁺/Ce³⁺ redox pairs are the active components in the degradation process in the presence of O₂, which served similar functions to the Mo⁶⁺/Mo⁵⁺ and Ce⁴⁺/Ce³⁺ redox pairs in a previous report [61].

To sum up, thermal catalytic reactions have been widely reported for the degradation of organic pollutants under dark ambient conditions in different systems in regard to the catalysts, model pollutants, reactive ROS, catalytic activity, experimental conditions, and degradation mechanism. A summary of the thermal catalysis used under dark ambient conditions reported in the field of environmental remediation is listed in Table 1. It should be noted that most of these studies are focused on the catalyst synthesis, characterization, catalytic activity evaluation, and investigation of the ROS responsible for model pollutant degradation. The toxicity of the final products, detailed pollutant degradation pathway, and interplay between catalyst and reactants/intermediates/products on the microscale are ignored ubiquitously. As such, future research should be dedicated to probing the microcosmic mechanism of thermal catalysis under ambient conditions with the aim of establishing guidelines for the development of the next-generation of thermal catalysts used for water treatment.

4. Reactions on the catalyst surfaces

4.1. Intrinsic active species and nature of the catalysts in thermal catalysis under dark ambient conditions

Thermal catalysis under dark ambient conditions for organic pollutant degradation occurs in varying reaction systems in light of the catalyst nature, catalytic activity, solvent chemistry, and target pollutant. This section aims to compare the catalytic systems reported to date in order to determine the intrinsic active species and correlate the composition/structure-performance relationships for these catalysts.

Based on previous reports, the catalytically active sites for thermal catalysis under dark ambient conditions involve variable-valence transitional metal ions, such as Cu, Ni, Fe, Bi, Ce, Co, and Mo. Their redox pairs are generally believed to play an important role in thermal catalysis under dark ambient conditions in water remediation. Interestingly, different degradation pathways have been proposed for similar catalytic systems in different studies. For example, lanthanum-nickel oxides (LaNiO_{3-δ} [35] and La₂NiO₄ [36]) have been identified to be catalytically active for organic pollutant degradation, whereas

La₂NiO₄ acts as an electron conductor in 4-CP degradation, the partial oxidation of Ni²⁺ in LaNiO_{3-δ} to Ni³⁺ after the reaction led to MO degradation with the synergistic role of lanthanum carbonate. Furthermore, there are sometimes more than one active site in thermal catalysts. This is especially true for composite materials, which tend to demonstrate higher catalytic activity due to the presence of multiple catalytically active sites. For instance, TiO₂ and PPy acting as active sites facilitate the separation of electrons and holes in Fe₃O₄ [68], promoting the generation of ROS. A similar synergistic benefit was also observed in a CaSe-graphene catalyst [65]. Moreover, foreign element doping in a parent catalyst is another useful strategy to introduce active sites that could significantly alter the catalytic degradation process in terms of the catalytic activity, degradation kinetics, and cycling performance. Chen et al. [34] substituted Sr with Ba, Ca, and Mg in SrCoO to give M_{0.5}Sr_{0.5}CoO materials. The results showed that the partial substitution of Ba, Ca, and Mg by Sr not only enhanced OII degradation and the cycling ability, but also changed the OII degradation kinetics. The doping of Ce in SrFeO resulted in various degradation mechanisms regarding the generation of ROS [40,41].

Overall, the active sites in the thermal catalysts under dark ambient conditions are generally transition metal-based materials that contain alterable oxidation states. This is due to the fact that the degradation of organic pollutants is a redox process for which a complete electron transfer pathway is prerequisite for a real catalytic process. It should be noted that doping with foreign elements in thermal catalysts can significantly alter the degradation process by affecting the electronic distribution in the active sites.

4.2. Reaction mechanisms

In heterogeneous catalytic reactions, the Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley-Rideal (ER) mechanisms have been proposed to describe the role of metal-based heterogeneous catalysts (Fig. 21). The LHHW mechanism has been widely employed to describe the heterogeneous catalytic degradation of organic pollutants. Two reacting species are pre-chemisorbed on the catalyst surface prior to the catalytic reaction [89]. The ER mechanism is less common in multi-phase systems used for surface catalysis as it involves the adsorption of one reactant on the already adsorbed oxidant on the catalyst surface [90]. In other words, one of the reactants is chemisorbed on the catalyst surface, while another reactant remains in the fluid phase. As a result, the reaction rate continues to increase as the surface coverage keeps increasing.

Apart from the two above-mentioned mechanisms and four mechanisms described in Section 2 for heterogeneous catalysis, care must be taken when drawing conclusions regarding thermal catalysis under dark ambient conditions. Direct experimental data is better in order to clearly illustrate the catalytic degradation mechanism (e.g., how and what ROS are generated, and their specific role in the degradation process). As such, in-situ advanced characterization techniques (isotopic tracer method, Raman, FTIR, XRD, EPR etc.) may provide insights into

Table 1

A summary of organic pollutant degradation processes operated in the dark at near room temperature and atmospheric pressure.

Catalyst	ROS	Model pollutants	Catalytic activity and conditions	Mechanism	Ref.
Ca _{0.5} Sr _{1.5} CuO ₃	OH•	OII	50 × 10 ⁻⁶ pollutant; 1 g L ⁻¹ catalyst; RT	SET	[33]
M _{0.5} Sr _{0.5} CoO ₃ (M = Ba/Ca/Mg)	OH•/ ¹ O ₂	OII	80% in 4 h; 20 × 10 ⁻⁶ pollutant; 1 g L ⁻¹ catalyst; RT	SET	[34]
LaNiO _{3-δ}	—	MO	94.3% in 4 h; 5 × 10 ⁻⁶ MO; 1.5 g L ⁻¹ ; RT	CWAO	[35]
La ₂ NiO ₄	OH•/O ₂ ⁻	4-CP/phenol/MO	95% TOC removal in 12 h; 5 × 10 ⁻⁶ 4-CP; 1.5 g L ⁻¹	SET	[36]
La ₄ Ni ₃ O ₁₀	—	MO	~100% in 3.5 h; 5 × 10 ⁻⁶ ; 1.5 g L ⁻¹	SET	[37]
SrFeO ₃	O ₂ ⁻	Bisphenol A/AO8	83% mineralization in 24 h (BPA); 100% discoloration in 1 h (AO8); 440 μm BPA; 150 μM AO8; 21 mM catalyst for BPA; 16 mM for AO8	MVK	[40]
Sr _{0.85} Ce _{0.15} FeO _{3-δ}	OH•/ ¹ O ₂	OII/RhB	95% in 6 h; 10 × 10 ⁻⁶ OII; 0.75 g L ⁻¹ ; 80 °C	CWAO	[41]
Mo-doped S/BiOCl	Hole/OH•/O ₂ ⁻	MB	96.5% in 1 h; 30 × 10 ⁻⁶ MB; 0.9 g L ⁻¹ catalyst; 40 °C	HC	[60]
SrTi _{1-x} Mn _x O ₃	—	RhB	50% in 4 h; 10 ⁻⁵ M RhB; 1 g L ⁻¹	MVK	[42]
CeGeO ₄	—	RhB/MB	100% in 24 h (MB) and 10 h (RhB); 3 × 10 ⁻⁶ RhB; 6 × 10 ⁻⁶ MB; 1.5 g L ⁻¹ ; RT	CWAO	[48]
MoZnAlO	¹ O ₂ /OH•	Cationic red GTL	80.1% in 1 h; 85 × 10 ⁻⁶ ; 2.72 g L ⁻¹ catalyst; pH 4	CWAO	[49]
Ni _x Fe _y Mn _z O	—	MO	83.8% in 40 h; 30 × 10 ⁻⁶ MO; 1 g L ⁻¹ catalyst; 50 °C	HC	[53]
MoZnAlO	—	Cationic orchid X-BL	94.6% in 10 min; 100 × 10 ⁻⁶ dye; 1 g L ⁻¹ ; RT	CWAO	[51]
MoZnAlO	¹ O ₂ /OH•	Cationic red GTL	90.9% in 1 h; 85 × 10 ⁻⁶ GTL; 2.72 g L ⁻¹ ; RT	CWAO	[50]
Mn-Si-Ca-Cu-Ni-O	OH•/O ₂ ⁻	MB	82.07% in 32 h; 40 × 10 ⁻⁶ MB; 1 g L ⁻¹ ; 35 °C	HC	[54]
NiCoMnO ₄	OH•/O ₂ ⁻ /holes	MB	75.9% in 10 h; 10 × 10 ⁻⁶ MB; 0.375 g L ⁻¹ ; 50 °C	HC	[55]
Mo-Cu-Fe-O	OH•	Cationic red GTL/crystal violet	90.4% (GTL) and 92.8% in 1 h (CV); 100 × 10 ⁻⁶ GTL; 1 g L ⁻¹ catalyst; RT	MVK (CWAO)	[52]
CuNiOS	Cu ⁺ /Cu ²⁺	MB/Cr(VI)	100% in 5 min; 10 × 10 ⁻⁶ ; 0.25 g L ⁻¹ ; RT	SET	[76]
Ce(IO ₃) ₄	¹ O ₂	RhB/MO/MB	100% in 50 min (RhB/MO); 58% in 8 h (MB); 10 × 10 ⁻⁶ dye; 1.5 g L ⁻¹ ; RT	CWAO	[57]
α-Fe ₂ O ₃	H ₂ O ₂ /•OH/O ₂ ⁻	Reactive brilliant blue X-BR	95% in 8 min; 20 × 10 ⁻⁶ dye; 0.1 g L ⁻¹ ; RT	HC	[58]
ZnO	OH•/O ₂ ⁻ /HO ₂ [•] /H ₂ O ₂	CR/MO	94.6% in 48 h (CR); 10 ⁻⁵ × 10 ⁻⁶ CR	SET	[59]
Mo-S-BiOCl	OH•/O ₂ ⁻ /HO ₂ [•] /hole	MB	96.5% in 1 h; 30 × 10 ⁻⁶ MB; 0.9 g L ⁻¹ ; 40 °C	HC	[60]
Fe-doped Sr ₂ Bi ₂ O ₅	Holes	MB	92.6% in 3 h; 20 × 10 ⁻⁶ MB; 0.875 g L ⁻¹ ; 50 °C	HC	[56]
Ce-doped MoO ₃	¹ O ₂ /OH•	Safranin-T	100% in 20 min; 0.3 g L ⁻¹ dye; 1 g L ⁻¹ catalyst; 25 °C	MVK (CWAO)	[61]
Ca _{0.5} Sr _{0.5} NiO ₃	H ₂ O ₂ /OH•	OII	97% in 5 min; 20 × 10 ⁻⁶ OII; 1 g L ⁻¹ ; RT	SET	[62]
Pt-TiO ₂ film	—	Formic acid	30% COD removal in 0.5 h; 15 mmol L ⁻¹ ; RT	CWAO	[64]
CaSe-graphene	OH•/O ₂ ⁻	RhB/MO	70% in 1 h (RhB) 100% in 1 h (MO); 10 ⁻⁵ M dye; 10 g L ⁻¹ catalyst; RT	HC	[65]
Cu ₂ (OH) ₃ NO ₃ /ZnO	OH•/H ₂ O ₂	MO	99% in 20 min; 0.5 g L ⁻¹ MO; 3 g L ⁻¹ ; RT	SET	[66]
N-doped P ₂₅ /F ₃ O ₄ -GO	OH•	CR	99.3% in 45 min; 150 × 10 ⁻⁶ CR; 0.87 g L ⁻¹ catalyst; pH 6; 25 °C	HC	[67]
Fe ₃ O ₄ @SiO ₂ @TiO ₂ @MIP	OH•/O ₂ ⁻ /hole	CR	93% in 25 min; 30 × 10 ⁻⁶ CR; 1 g L ⁻¹ catalyst; 25 °C; pH 6.1	HC	[68]
Pt-HCa ₂ Nb ₃ O ₁₀	—	MO	100% in 250 min; 0.667 g L ⁻¹ catalyst; 25 °C	CWAO	[69]
ZnAl-LDH/H ₃ PMo ₁₂ O ₄₀	OH•/O ₂ ⁻	MO	74.2% in 10 min; 0.1 g L ⁻¹ MO; 0.8 g L ⁻¹ catalyst; 25 °C	SET	[70]
Co ₂ O ₃ -TiO ₂	O ₂ ⁻	2-Naphthol	80% in 2 h; 10 μmol L ⁻¹ ; 2 g L ⁻¹ catalyst; 323 K	SET	[71]
M ₂ Mo ₄ O ₁₃ /α-MnO ₃ (M=Li/Na/K)	OH•	Cationic red GTL	100% in 30 min; 200 × 10 ⁻⁶ dye; 0.33 g L ⁻¹ catalyst; RT	CWAO	[72]
Na ₂ Mo ₄ O ₁₃ /α-MoO ₃	OH•	cationic red GTL	100% in 0.5 h; 200 mg L ⁻¹ dye; 0.17 g L ⁻¹ catalyst; 30 °C	CWAO	[73]
Alkali-treated Pt	-OH/OH	HCHO	90% in 1 h; 0.1 g catalyst; RT	LHHW	[75]
Pt/SnO _x	Active O	HCHO	87% in 1 h; 0.1 g catalyst; RT	LHHW	[76]
Pt/ZnO	Active O	PhCH ₂ OH	94.1% in 10 h; 0.1 g catalyst; 26 °C	LHHW	[78]
ZnO/MoO ₃ /SiO ₂	OH•/H ₂ O ₂ /O ₂ ⁻	Safranin T	95.3% in 25 min; 0.3 g L ⁻¹ ST; 10 g L ⁻¹ catalyst; RT	SET	[83]
CuO-MoO ₃ -P ₂ O ₅	•OH	MB	99.26% in 10 min; 0.3 g L ⁻¹ MB; 13.3 g L ⁻¹ catalyst; pH 5; 35 °C	SET	[84]
Zn _{1.5} PW ₁₂ O ₄₀	—	Safranin T	80% in 6 h; 34.1 × 10 ⁻⁶ ST; 1 g L ⁻¹ catalyst; RT	CWAO	[85]
ZnO/MoO ₃	—	Safranin T	98% in 18 min; 0.3 g L ⁻¹ dye; 1 g L ⁻¹ catalyst; RT	CWAO	[86]
Fe ₂ O ₃ -CeO ₂ -TiO ₂ /γ-Al ₂ O ₃	OH•/R•/RO•	MO	98.09% in 2.5 h; 0.5 g L ⁻¹ MO; 30 g L ⁻¹ catalyst; RT	FRCAO (CWAO)	[87]
Zn _{1.5} PMo ₁₂ O ₄₀	OH•/R•/RO•	Safranin-T	98% in 40 min; 10 × 10 ⁻⁶ dye; 1 g L ⁻¹ catalyst; RT	FRCAO (CWAO)	[88]

the catalytic role of the catalysts, generation and fate of ROS, interactions between the pollutants and catalysts, and detailed degradation pathways. It is also highly recommended that the separate roles of each of the components in the organic removal process are investigated to conclude the effect of other fac-

tors (e.g., pollutant physisorption) on the evaluation of the catalytic activity.

4.3. Critical methods used to determine the reactive species

Fig. 21. An illustration of the LHHW and ER mechanisms.

It is widely reported that ROS, such as hydroxyl ($\cdot\text{OH}$), superoxide anion ($\text{O}_2^{\cdot-}$), singlet oxygen ($^1\text{O}_2$), and hydroperoxyl ($\text{HO}_2^{\cdot-}$), are produced in photocatalysis, the Fenton reaction, sulphate-based AOPs, and CWAOP used for the degradation of organic pollutants. Interestingly, ROS are also generated in thermal catalysis under dark ambient conditions leading to the degradation of organic pollutants. Hence, the determination of ROS in thermal catalysis under dark ambient conditions plays a pivotal role in understanding the thermal catalysis process. Given the similarity between thermal catalysis under dark ambient conditions and the aforementioned AOPs, the methods used to identify ROS in other AOPs can be adopted in thermal catalysis under dark ambient conditions.

The most popular strategy is the employment of radical quenching experiments using suitable radical quenchers and electron paramagnetic resonance (EPR) techniques. Radical quenchers will indirectly provide information on the ROS responsible for the degradation process by reacting with the corresponding radicals, while EPR displays the characteristic peaks of certain radicals. However, one must take care while determining the ROS responsible for thermal catalysis under dark ambient conditions. This is because both methods have limitations in exclusively identifying the radicals generated. For example, 2,2,6,6-tetramethyl-4-piperidone (TMP) is widely used as the trapping agent for singlet oxygen in EPR due to the characteristic triplet peaks. Whereas, the reaction between superoxide radical and TMP may induce similar triplet peaks to singlet oxygen [91]. As such, the EPR technique using TMP as the trapping agent cannot exclusively distinguish between these two reactive species. Furthermore, the addition of the singlet oxygen trapping agent TMP (alkaline in nature) may mislead the results as other radicals ($^1\text{O}_2/\text{O}_2^{\cdot-}$) could be generated due to the variation in the pH environment. Additionally, for radical quenching experiments, a single adopted quencher used for a certain radical may have a quenching effect on other radicals. This is especially true since the ROS generated are highly oxidative and could indiscriminately interact with sensitive quenchers, such as sodium azide, which is widely used as a singlet oxygen quencher [92]. Besides, one must be careful while interpreting the quenching results using a complexing agent (e.g., EDTA, EDTA-2Na) as a hole scavenger because it may cease the reaction via wrapping the active sites of the catalysts via a complexation effect instead of its hole scavenging effect. Hence, care must be taken when identifying the ROS based on the simple EPR method or chemical quenching because other reactive species may affect the results as well.

Therefore, other techniques such as direct fluorescence, fluorescence probes, and chemiluminescence should be considered for detecting ROS in thermal catalysis under dark ambient conditions [20]. In conclusion, it is recommended that diverse techniques are integrated when determining the generation and pathway of ROS involved in the thermal catalytic reaction under dark ambient conditions.

5. Limitations of thermal catalysis under dark ambient conditions in environmental remediation

5.1. Poor applicability and limited mineralization

As wastewater from domestic and industrial sewage generally contains diverse organic pollutants, practical catalysts should possess good applicability for differing contaminants in various systems. However, most of the thermal catalysts reported to date merely focus on a single model pollutant and ignore their applicability toward other pollutants under dark ambient conditions [33,35,69]. Only a limited number of studies have investigated the catalytic role for multiple organic pollutants [36,40]. The results show that significant selectivity exists for the degradation of cationic dyes and anionic dyes using Ce-doped SrFeO [41], ZnO [59], and $\text{La}_4\text{Ni}_3\text{O}_{10}$ [37] catalysts, all preferably degrading anionic dyes in contrast to cationic dyes. Furthermore, most studies selected colored dyes instead of other more refractory colorless compounds as the model pollutants. This probably originates from the fragile nature of dyes (especially azo dyes containing weak $-\text{N}=\text{N}-$ bonds). Besides, most pollutants are degraded into smaller molecular weight by-products with most organic carbon remaining in the treated solution [33,64]. Some catalysts even display negligible mineralization ability and the observed discoloration is purely due to the destruction of the $-\text{N}=\text{N}-$ bonds, leaving practically all the organic carbon in the residual degradation products [34,62].

Overall, further studies should be made to address the obvious selectivity issues and enhance the mineralization capability of thermal catalysts under dark ambient conditions. Measures that can be taken include combining other AOPs with thermal catalysis to achieve the synergistic effect of multiple technologies. A combination of thermal catalysis with photocatalysis has already led to enhanced catalytic performance in wastewater treatment [42].

5.2. Facile deactivation

Stability is one of the primary parameters for practical catalysts in water remediation. Unfortunately, some of the thermal catalysts used for pollutant degradation under dark ambient conditions reported to date suffer from catalyst deactivation due to the irreversible reduction, oxidation, blockage, or breakdown of the active sites in the catalysts. Taking $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{NiO}$ as an example, the irreversible oxidation of Ni^{2+} to Ni^{3+} after the reaction causes facile catalyst deactivation and poor cycling performance for OII degradation [62]. Another example is the partial reduction of Mn^{4+} in the $\text{SrTi}_{0.95}\text{Mn}_{0.05}\text{O}_3$

catalyst during the thermal oxidation of RhB [42].

The photocorrosion of catalysts is common in photocatalysis arising from the accumulated electrons in the conduction band or holes in the valence band. Thus, the same concerns should be raised for thermal catalysts to avoid deactivation and prolong their durability. As electron transfer is of pivotal significance in catalysis, strategies that can accelerate electron transfer will benefit the overall catalytic reaction by enhancing charge carrier separation, ROS formation, and catalyst regeneration. For instance, the addition of CeO₂ facilitates the regeneration of MoO₃ by acting as an effective oxygen transfer agent [61]. TiO₂ and PPy enhance electron transfer in Fe₂O₃ to allow for the facilitated generation of ROS during the degradation of congo red [68]. A similar role was also observed for graphene in RhB degradation using CaSe as a thermal catalyst under dark ambient conditions [65].

6. Summary and outlook

Currently, a number of studies have reported the thermal catalytic degradation of organic pollutants in the field of water remediation under dark ambient conditions. Unlike other AOPs (Fenton reaction, photocatalysis, sulfate radical-based AOPs, ozonation, and electrolysis), which generally require the addition of external stimuli (H₂O₂, O₃, and peroxysulphate) or extra energy input (light, ultrasound, and microwave), thermal catalysts can be employed under dark ambient conditions without adding external energy or chemical oxidants to achieve the facile degradation of organic pollutants. Hence, it may find huge applications in the treatment of organic pollutant contaminated wastewater in problematic locations such as underground and in soil where other AOPs are strictly limited.

A couple of dark catalysis mechanisms have been proposed and summarized in the present review. However, some of the mechanisms for thermal catalysts under dark ambient conditions reported to date remain ambiguous and controversial due to the lack of effective in-situ characterization techniques used to characterize the catalysts, detect real-time ROS, and determine the specific degradation pathways. It is very demanding to provide a detailed mechanistic description of catalytic reactions to elucidate the specific reaction process and provide further guidance for catalyst design. Thus, systematic studies are encouraged including identifying the intrinsic catalytic sites, the generation and fate of the ROS involved, charge transfer, and interactions among the target contaminants/intermediates/catalysts to advance the promising application of thermal catalysis under dark ambient conditions in wastewater treatment. Combined techniques (e.g., radical trapping experiment, EPR, and fluorescence techniques) should be used to identify the ROS due to the complex and variable physicochemical nature of the reaction systems.

It should be pointed out that previous reports have mainly focused on dye contaminants, which have a relatively moderate redox potential. Investigations on other recalcitrant pollutants are very limited. Some of the thermal catalysts used for dye degradation under dark ambient conditions reported to date demonstrate limited mineralization abilities. Sometimes the

decolorization of the dye solutions studied was simply due to the destruction of the azo bonds present in the dye molecules, whereas complete mineralization was not achieved. These may provide more research opportunities toward the development of novel thermal catalysts used for the decomposition of refractory organic pollutants under dark ambient conditions.

There is no doubt that significant progress has been achieved in the thermal catalytic degradation of organic pollutants in water treatment. Many advances have been accumulated for the design and fabrication of efficient thermal catalysts under dark ambient conditions. The rich knowledge obtained in this area can be used toward developing more efficient and robust thermal catalysts for the facile degradation of refractory organic pollutants in the dark at room temperature and atmospheric pressure.

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Graphical Abstract

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Thermal catalysis under dark ambient conditions in environmental remediation: Fundamental principles, development, and challenges

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Dark ambient catalysis, which can be grouped into four categories based on reaction mechanisms, plays an important role in the field of environmental remediation in terms of straightforward operation and cost saving.

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常温常压黑暗条件下用于环境修复的热催化：基本原理、发展和挑战

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摘要: 近年来, 对热催化剂在黑暗常温常压和不添加其他化学品和能源的条件下降解有机污染物的研究取得了长足的进步, 受到了学术界和工业界的广泛关注. 与其他高级氧化过程相比, 该方法在处理生活和工业废水时具有操作简便和节约成本等优势. 但截止目前, 对其催化机理的研究尚有争议. 本综述首次系统总结了目前报道的各种热催化机理, 可为理性设计新型高效热催化剂提供理论指导, 从催化材料、催化活性和催化机理三个方面提出发展热催化剂过程中面临的挑战, 并对其在黑暗氛围条件下处理污染废水的可行性进行了展望.

和传统的多相催化反应一样, 黑暗氛围条件下发生的热催化反应也分为五步, 即反应物扩散到催化剂表面、反应物吸附到催化剂表面、发生在催化剂表面的催化反应、产物从催化剂表面脱附、以及产物从界面区域扩散到主体溶液。根据第四步反应过程的不同, 可将黑暗氛围条件下的热催化反应分为四类: 表面电子传递机理、跳跃传导模型机理、Mar-van-Krevelen机理、以及自由基链自氧化机理。

对于表面电子传递机理, 吸附的有机污染物将自身电子通过催化剂导带或氧化还原对注入催化剂, 由此得到被捕获电子和被部分氧化的有机污染物阳离子。随后被捕获电子与吸附氧反应生成活性氧物种, 由其导致有机污染物的降解。跳跃传导模型机理类似于光催化机理, 当催化剂受到等于或高于禁带宽度的能量时, 自身的价带电子被激发到导带, 在价带留下空穴。空穴可直接氧化水生成羟基自由基。同时, 导带电子可以和吸附氧反应生成活性氧物种, 这些活性氧物种实现有机分子的热催化降解。Mar-van-Krevelen机理包含催化剂晶格氧化有机污染物和催化剂的氧化再生。对于该过程, 催化剂类似于氧气传导媒介。自由基链自氧化机理中, 有机物质(RH)与催化剂相互作用生成 $R^{\bullet}$ 、 H^+ 和还原态的催化剂, 还原态的催化剂可通过与吸附氧反应再生, 同时生成 $HO^{\bullet}$, 而 $HO^{\bullet}$ 又可与RH反应得到 $R^{\bullet}$ 和水。 $R^{\bullet}$ 可通过与氧反应生成 $ROO^{\bullet}$, 由此引发自由基链自氧化反应。

由于反应体系复杂多变的特性, 对于黑暗氛围的热催化反应需进行系统的研究以明确本征催化位点, 在确定涉及活性氧物种和表征催化性能时, 建议采用多种技术手段, 研究活性氧物种的产生和消亡、电子传递、以及目标污染物/中间产物和催化剂的相互作用, 以便准确了解反应进程、阐释反应机理、促进其在废水处理中的应用前景。除了易降解的有机染料, 应尽可能的尝试其他难降解有机污染物, 考察热催化剂催化性能的普适性。

关键词: 黑暗氛围下的热催化; 反应机理; 高级氧化过程; 废水处理; 有机污染物降解

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