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Review

When bimetallic oxides and their complexes meet Fenton-like process

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ABSTRACT

The heterogeneous Fenton-like reaction is an advanced oxidation process, which is widely recognized for its efficient removal of recalcitrant organic contaminants. In recent years, the construction of efficient and reusable heterogeneous Fenton-like catalysts has been extensively investigated. Recently, the use of bimetallic oxides and their complexes as catalysts for Fenton-like reaction has attracted intense attention due to their high catalytic performance and excellent stability over a wide pH range. In this article, the fundamental mechanisms of Fenton-like reactions were briefly introduced. The important reports on bimetallic oxides and their complexes are classified in detail, which are mainly divided into Fe-based and Fe-free bimetallic catalysts. We then focused in depth on the performance of their respective applications in Fenton-like reactions. Special consideration has been given to the respective contributions and synergistic mechanisms of the two metals in catalysts. Overall, it is concluded that synergistic effect of the two metals in the bimetallic catalyst can boost the utilization of hydrogen peroxide, provide adequate accessible active sites, which are all beneficial to improve catalytic performance. Finally, the current challenges in this field were proposed. Our review is expected to provide help for the application of bimetallic oxides and their complexes.

1. Introduction

A variety of persistent and biologically refractory chemicals were released into the aquatic environment on the daily basis, leading to increased surface and groundwater pollution worldwide and causing global concern (Liu et al., 2017; Richardson and Kimura, 2020). Moreover, these recalcitrant organic contaminants pose a tremendous threat to ecosystems and human health (Liu et al., 2020a, 2020b, 2020c, 2018a, 2018b). The removal of refractory contaminants usually requires basic water treatment technologies (Jiang et al., 2018; Yang et al., 2021), such as adsorption technology (Wang and Wang, 2019), ozonation (Wang and Chen, 2020) and so on. However, the possible shortcomings of these technologies in operation, such as poor selectivity and inability to operate continuously, limit their practical application. Therefore, it is necessary to develop an effective method to eliminate recalcitrant organic contaminants in wastewater.

Advanced oxidation processes (AOPs) can produce reactive oxygen species (ROSs) including hydroxyl radicals (•OH), superoxide anion radicals ($O_2•^-$) and singlet oxygen ($^1O_2$), which have been proven to catalytically degrade organic contaminant in aqueous solutions in a short treatment time (Cheng et al., 2017; Yang et al., 2016). Since Henry J. Fenton (Fenton, 1884) discovered that hydrogen peroxide (H_2O_2) could be activated by ferrous ions (Fe(II)) to oxidize tartaric acid in 1894, Fenton and its related reactions have gained continuous interest in fields of environmental remediation (Huang et al., 2017a, 2017b; Pignatello et al., 2007). In the classical Fenton reaction (Eq. (1)), Fe (II) catalyzes the decomposition of H_2O_2 to produce highly active •OH. The •OH generated from Fenton reaction can initiate the elimination of organic contaminants by hydrogen abstraction (Eq. (2)) or hydroxyl addition (Eq. (3)), and then convert organic contaminants to less harmful compounds or even completely decompose into non-toxic products such as CO_2 and H_2O (De la Cruz et al., 2012; Li et al., 2019; Xiao et al., 2019).

$$\mathrm{Fe(II)}+H_2O_2\rightarrow \mathrm{Fe(III)}+OH^-+\bullet OH \tag{1}$$

$$RH+\bullet OH\rightarrow H_2O+R\bullet\rightarrow \text{degraded products} \tag{2}$$

$$\text{R(organic contaminants)}+\bullet OH\rightarrow \bullet ROH\rightarrow \text{degraded products} \tag{3}$$

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The classic Fenton system holds many advantages, including low cost and wide application range (Chen et al., 2021; Liu et al., 2021; Wang and Zhuan, 2020). However, the applicability of homogeneous Fenton reaction has some shortcomings, such as the need of strong acid conditions ($pH < 3$) (Pignatello, 1992), a large number of sludge generation (Buxton et al., 1988), inevitable metal leaching, as well as difficult separation and recovery of metal ions (Katsumata et al., 2005). To solve these problems, heterogeneous Fenton-like system has been developed. In recent years, huge amounts of materials have been employed in heterogeneous Fenton-like processes (Liu et al., 2019), such as transition metal oxides, clays and carbon materials (Nie et al., 2010). However, these catalysts often require light, ultrasound or electricity if they want to achieve better catalytic performance. The demand for specific equipment and energy consumption will increase the cost of the degradation process (Zhang et al., 2010). Therefore, the development of novel heterogeneous Fenton-like catalysts with high removal efficiency, limited metal ion leaching, high stability for a prolonged duration and no need for external energy is of great importance but challenging.

The occurrence of bimetallic oxides has brought new opportunities for the development of heterogeneous Fenton-like catalysts, owing to their higher reactivity and stability than the corresponding monometallic oxides (Chen and Wang, 2021). In order to achieve better catalytic properties, some researchers have focused their efforts on loading bimetallic oxides on supports. This also signifies a chance to put other functionalities of composite units to synthesize Fenton-like catalysts with ultrahigh performance. Considering this, porous materials have been introduced as excellent supports of bimetallic oxides to obtain highly efficient bimetallic oxide complexes. In some cases, the interaction and synergy occur between bimetallic oxide particles and support materials, exerting positive effects on Fenton-like catalytic performance.

Since the discovery of bimetallic oxide in the late 1990s (Kul Ryu et al., 1999), the research for wastewater purification through bimetallic oxides and their complexes has been a topic of great interest. Several review papers (Costa et al., 2006; Liu et al., 2021; Wang and Tang, 2021a, 2021b, 2021c) have already mentioned the applications of bimetallic oxides and their complexes in Fenton-like. As early as 2014, Pouran et al. (2014) summarized the progress in the synthesis of Fe oxide-doped transition metals, and concluded that Fe-based bimetallic oxides are expected to efficiently degrade a variety of organic pollutants in the Fenton reaction. More recently, Wang and Tang (2021a, 2021b, 2021c) summarized the preparation and characterization methods of Fe-based catalysts as well as their applications in Fenton-like catalytic degradation. However, reviews outlining the bimetallic oxides and their complexes for Fenton-like process and the related mechanism have not been available. Significant reports (Qin et al., 2020; Zhang et al., 2020b) have mentioned that the synergistic effects of bimetallic oxides and their complexes effectively integrated their respective multiple advantages and improved the reactivity of pure transition metal oxides. However, to the best of our knowledge, the respective contributions and underlying synergistic mechanisms of two metals in bimetallic oxides are far from being well understood and deserve further investigations. Therefore, a detailed review of bimetallic oxides and their complexes in Fenton-like catalysis can provide new theoretical ideas and promote the development of Fenton-like catalysts.

Herein, we provide an overview of bimetallic oxides and their complexes for Fenton-like catalysis. Firstly, the fundamental mechanism of the Fenton-like processes is briefly introduced. Secondly, we outline a summary on the application of different types of bimetallic oxides and their complexes-based Fenton-like processes for degrading recalcitrant organic contaminants. Then, the respective contributions and synergistic mechanisms of the two metals in catalytic process are discussed and summarized. Special attention has been paid to the exact roles of two metals of bimetallic oxides and their complexes in Fenton-like processes. Finally, based on the current research progress in this field, the challenges and future development directions are proposed.

2. The fundamental mechanisms of Fenton-like reaction

In the classical Fenton reaction, the highly oxidative •OH formed by the reaction of H_2O_2 and Fe(II) under strong acid can quickly convert most stubborn organic contaminants to CO_2 and H_2O in a non-selective way (Cheng et al., 2019; Wang et al., 2018a, 2018b, 2018c). Similar to the classical Fenton reaction which involves Fe(II) as catalyst, many other transition metal ions (e.g., Cuprum (Cu(II)), Cobalt (Co(II)), Manganese (Mn(II)), Cerium (Ce(III)), Aluminium (Al(III)) and Chromium (Cr(III))) can also activate H_2O_2 to generate •OH, which are called Fenton-like reactions (Bokare and Choi, 2014). The related reaction mechanism for the Fenton-like reactions is summarized in Fig. 1. The rate-limiting step of H_2O_2 decomposition is also the reduction of transition metals (summarized by Eq. (4)). Subsequently, the reduced transition metals are reoxidized by H_2O_2 while forming the highly active •OH (summarized by Eq. (5)). It is well known that there are two kinds of •OH, namely free •OH ($\bullet OH_{free}$) and surface-bound •OH ($\bullet OH_{ads}$) (Xu and Wang, 2012). Many transition metals can undergo a redox cycle in the presence of H_2O_2 to generate $\bullet OH_{ads}$, which behave similarly to Fe in the Fenton-like reaction (Luo et al., 2010). Nevertheless, the dissolved transition metal ions incline to disperse into solution and decompose H_2O_2 to generate $\bullet OH_{free}$ through a chain reaction, thereby significantly promoting the efficiency of heterogeneous Fenton-like reaction system (Eq.(3)), which will be described in detail below.

$$M(X+1)+H_2O_2 \rightarrow M(X)+H^+ + \bullet OOH \tag{4}$$

$$M(X)+H_2O_2 \rightarrow M(X+1)+OH^- + \bullet OH \tag{5}$$

It is well known that the reduction of Fe(III) by H_2O_2 is rate-limiting step in the Fe-based Fenton-like process (Ju et al., 2015; Rahim Pouran et al., 2014). In recent years, it has been reported that Fe-free metals with multiple oxidation states can effectively decompose H_2O_2 to produce •OH (Chen and Wang, 2019; Dong et al., 2020), and these low-valent transition metals can reduce Fe(III) in the bimetallic system, thereby accelerating the regeneration of Fe(II). In addition, a significant interfacial interaction may occur between the added metal and Fe due to their different redox properties. In fact, it was confirmed that the combination of two different transition metals provided opportunities for reducing metal sites, and played a vital role in promoting the reduction of Fe(III) to Fe(II). In addition, the redox cycle existing between two different transition metals greatly enhances the interfacial electron transfer of bimetallic oxides and their complexes, thereby increasing the generation of •OH and the degradation efficiency of organic pollutants. It can be expected that the introduction of active non-Fe metals into

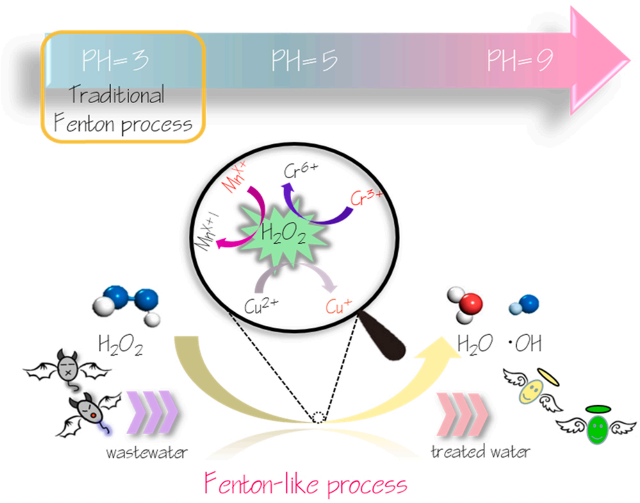

Fig. 1. Reaction mechanism for the Fenton process.

Fe-based catalysts not only provides more active sites for the formation of •OH, but also expand the working pH range of Fenton-like. For example, Tang and Wang (2020) prepared bimetallic material (Fe_x-Cu_{1-x}(BDC)) for heterogeneous Fenton-like oxidation of sulfamethoxazole (SMX). The results suggested that the Fenton-like system exhibited high catalytic activity in a wide pH range (4.0–8.6) owing to the synergy of Fe and Cu.

In the Fenton-like reaction, Fe(VI), as a new oxidant, will self-decay in water with pH lower than 9 to form Fe(V), Fe(IV), Fe(III), Fe(II) (Zhu et al., 2020). Thus, the reactive intermediates (high-valent Fe species) produced by the reaction of Fe(II) and H_2O_2, namely Fe(IV), Fe(V) and Fe(VI), all contribute significantly to the oxidation of organic pollutants (Lee et al., 2014). It has recently been confirmed that Fe(VI) generates Fe (V) through the one-electron transfer mechanism, or Fe(IV) is generated by the two-electron transfer mechanism (Sharma, 2010). Then, the newly formed Fe(V)/Fe(IV) helps to degrade organic pollutants in Fe (II)/Fe(III)-oxidant system, which is a potential active oxidant to promote the oxidation of organic pollutants. Like high-valent Fe, Cu-based species (Cu(III)) are strong oxidants produced during the activation of H_2O_2 (Lee et al., 2018). The redox potential of Cu(III)/Cu(II) (2.3 V) is slightly higher than Fe(VI) (2.2 V). Therefore, the high oxidation state of Cu(III) as an oxidant exhibits high activity and selective catalytic oxidation in the degradation of organic pollutants.

In order to make up for the low catalytic activity of traditional Fenton-like reactions, bimetallic oxides and their complexes with dual-reaction centers have been developed to improve the degradation efficiency (Lyu et al., 2018). In the bimetallic oxide/H_2O_2 system, due to the different electronegativity of the doped metal ions, which creates an inhomogeneous distribution of electron density, the electron conversion between the two reaction centers easily forms active dual-reaction center, that is, the poor/rich electronics centers. The organic matter and H_2O_2 are clustered around the electron-poor center and electron-rich center respectively. In the catalytic process, the electron-rich center reduces H_2O_2 to generate ROS (e.g., $^1O_2$, $O_2\bullet^-$/$HO_2\bullet^-$ and •OH), while the electron-poor center adsorbs contaminants and intermediates, and then transfers the electrons provided by the organics to the electron-rich center. Therefore, the introduction of different electronegative metals to form electron-rich centers and electron-poor centers can improve catalytic activity and H_2O_2 utilization efficiency.

In the experiments, the bimetallic oxides and their complexes were added to the heterogeneous catalytic system in solid form. Therefore, the Fenton-like process involves solution reactions and interfacial reactions. The different reactions in the Fenton-like system contribute to the degradation of organic pollutants by H_2O_2 and bimetallic catalysts. It is well known that Fe(II) reacts with H_2O_2 to generate •OH and at the same time Fe(III) is generated. Fe(II) produced by these reactions can participate in Fenton-like reactions to enhance the generation of •OH. Similarly, Cu(I) in the presence of H_2O_2 can also generate •OH and produce Cu(II) (Yamaguchi et al., 2018). Similar to the reaction trajectory of Fe, both monovalent and divalent oxidation states of Cu can undergo continuous Fenton-like reactions with H_2O_2 (Ju et al., 2015).

In Fenton-like catalysis, doping with foreign metals can accelerate electron transfer and promote the reduction of high-valence metal ions, thereby activating H_2O_2 faster to generate highly reactive species such as •OH, and at the same time increasing the number of accessible reaction sites by improving structural properties (Dai et al., 2017). According to the literatures (Kwan and Voelker, 2002; Pera-Titus et al., 2004; Pham et al., 2009), the decomposition of H_2O_2 by bimetallic oxides and their complexes usually includes two situations under different pH conditions. Under lower pH conditions ($pH < 4.5$), the process is controlled by the redox cycle of transition metal ions (like dissolved Fe (III)/Fe(II)), which are released from solid catalysts due to acidic pH conditions (de Souza et al., 2010). Therefore, the solubility of solid catalyst has a great impact on the H_2O_2 activation at lower pH (Hammouda et al., 2016). On the contrary, at neutral and alkaline pH values, the contribution of dissolved metal ions to the H_2O_2 decomposition is negligible (Pham et al., 2012). Taking the traditional Fe ion as an example, under neutral and alkaline pH conditions, the increase in the rate constant of Eq. (1) with increasing pH was attributed to the reaction of hydrolyzed $FeOH^+$ with H_2O_2 (Pignatello et al., 2006). Thus, the activation of H_2O_2 at neutral and alkaline pH values may be a surface catalytic process (Pham et al., 2009).

3. Fe-based bimetallic catalyst for heterogeneous Fenton-like reaction

Among various types of bimetallic oxides and their complexes reported, Fe-based bimetallic oxides and their complexes showed tremendous potential due to easy availability of raw materials, low cost and high removal efficiency (Cai et al., 2017; Li et al., 2017a, b,c). Some Fenton-like processes for decomposition of organic pollutants by Fe-based bimetallic oxides and their complexes are presented in Table 1. The synergistic interactions between Fe and other transition metals (such as Cu, Ni, and Mn) have been widely investigated. At the same time, several methods such as introducing other metals and adding supports to improve the performances of Fe-based bimetallic catalysts have become a hot research field (Li et al., 2015a, 2018a, 2018b, 2018c). In the Fe-based bimetallic catalyst/H_2O_2 system, the degradation efficiency is mainly improved by four effective ways: (i) accelerating the regeneration of Fe(II) on catalyst surface; (ii) forming oxygen vacancies (OVs); (iii) improving structural properties; and (iv) introducing supports.

3.1. Struggle with ferrous ion (Fe(II)) oxidation

It is well known that the regeneration rate of Fe(II) is the rate-limiting step of the Fenton-like reaction (Bokare and Choi, 2014), which may influence the process of H_2O_2 activation and contaminants degradation. However, the low reduction rate ($(1.0–3.0) \times 10^{-3}$ $M^{-1}s^{-1}$) of Fe(III) to Fe(II) in the Fe(III)/Fe(II) redox cycle of pure Fe oxide largely limits the reduction efficiency (Georgi et al., 2016; Salgado et al., 2017). Study has confirmed that the doping of other metals was highly beneficial for degradation performance by improving the efficiency of electron transfer and redox cycling of metal ions (Hammouda et al., 2017). For example, Luo et al. (2010) prepared $BiFeO_3$ with Fe and Bi doping and used it as a heterogeneous Fenton-like catalyst to degrade Rhodamine B (RhB). The results showed that the degradation rate of RhB in the $BiFeO_3$/H_2O_2 system was about 20 times higher than that of the Fe_3O_4 catalyst at similar conditions. In most cases, the addition of active metal ions not only initiates the Fenton-like process automatically, but also greatly accelerates Fe(II) regeneration and interface electron transfer through conjugation of redox pairs (He et al., 2016). This is mainly because the regeneration of Fe(II) can be driven by metal active sites as electron donors (Huang et al., 2017a, 2017b). As early as in 2014, Zhang and co-workers (Zhang et al., 2014) found that $CuFeO_2$/H_2O_2 system exhibited pronounced Fenton-like reactivity than pure Cu_2O/H_2O_2 and Fe_3O_4/H_2O_2 systems. The high removal rate of bisphenol A (BPA) was mainly ascribed to the synergistic functions of Cu and Fe. It increased the number of adsorption and active sites, promoted the surface Fe cycle through effective electron transfer, accelerated the reduction rate of Fe(III), and presented positive effects on the effective generation of •OH (Zhang et al., 2014). Similar results were reported by many other researchers. In a subsequent study, the degradation performance of N,N-diethyl-phenylenediamine (DPD) in CuO/Fe_2O_3/H_2O_2 system was significantly higher than that in CuO/H_2O_2 or Fe_2O_3/H_2O_2 systems (Karthikeyan et al., 2016). It was observed that there were highly dispersed CuO and Fe_2O_3 in the catalyst. The analysis suggested that the effective reduction of Fe(III) by Cu promoted the decomposition of H_2O_2 into •OH, which contributed to the remarkable increase of DPD removal efficiency (Karthikeyan et al., 2016; Wang et al., 2015).

More reports have also confirmed that Fe-based bimetallic oxides

Table 1
Summary of some relevant studies on the application of bimetallic oxides and their complexes in Fenton-like reaction.

Catalyst	Pollutants	H_2O_2	Reaction conditions	Removal efficiency (%)	Leached ions	Reusability	Suitable pH	Refs.
$CuFeO_2$	BPA	20.0 mmol/L	$pH_0 = 5.0$, [Catalyst] = 1.0 g/L, [BPA] = 0.1 mmol/L	100 (120 min)	Fe(III):0.05 mg/L, Cu^{2+}:0.41 mg/L	6 successive runs without obvious loss of activity.	4–8	(Zhang et al., 2014)
$MnFe_2O_4$	NOR	200 mmol/L	T = 25 ℃, $pH_0 = 6.6$, [Catalyst] = 0.6 g/L, [norfloxacin] = 10 mg/L	90.6 (180 min)	Mn、Fe < 1.0 mg/L	No significant reactivity loss after 5 cyclic runs.	7.5–8	(Wang et al., 2018a, 2018b, 2018c)
$FeCeO_x$	Diclofenac	3.0 mmol/L	T = 25 ℃, $pH_0 = 5.0$, [Catalyst] = 0.5 g/L, [Diclofenac] = 0.07 mmol/L	84 (40 min)	Ce、Fe < 0.1 mg/L	Good performance even after 5-cycle runs.	4–5	(Chong et al., 2017)
Fe_3O_4/CeO_2	4-chlorophenol		T = 30 ℃, $pH_0 = 3.0$, [Catalyst] = 2.0 g/L, [4-chlorophenol] = 0.78 mmol/L	100 (30 min)	Fe:11.8 mg/L	Catalytic activity decreased after 6 runs.		(Xu and Wang, 2012)
$LaFeO_3$	SMX	23 mmol/L	T = 30 ℃, $pH_0 = 6.48$, [Catalyst] = 1.4 g/L, [SMX] = 3 mg/L	100 (120 min)		10 successive runs without obvious loss of activity.	5.5–7.14	(Nie et al., 2015)
$LaFeO_3$, $BiFeO_3$	Phenol, MTBE	3.0 g/L	T = 40 ± 2 ℃, $pH_0 = 7$, [Catalyst] = 0.1 g/L, [Phenol] = 25 mg/L, [MTBE] = 50 mg/L	> 95 (24 h)	Fe < 1 μg/L, Bi < 0.2 μg/L	No obvious loss of catalytic activity after 4 cycles.	5–7	(Rusevova et al., 2014)
$BiFeO_3$	RhB, Phenol, MB	10.0 mmol/L	T = 25 ℃, $pH_0 = 5$, [Catalyst] = 0.5 g/L, [RhB] = 10.0 μmol/L		Fe < 0.9 mg/L	Retained its original activity after 5 runs.	3–8	(Luo et al., 2010)
$Fe_3O_4/FeMnO_x$	MB	30%, w/w	T = 25 ± 1 ℃, $pH_0 = 6.5$, [Catalyst] = 0.1 g, [MB] = 25 mg/L	90 (250 min)	Mn: 0.12 mg/L, Fe: 1.0 mg/L	Used catalyst did not exhibit any obvious activity loss	3.5–9	(Xing et al., 2011)
Fe/Cu/MCM-41	phenol	0.049 mol/L	T = 60 ℃, $pH_0 = 4$, [Catalyst] = 1.5 g/L, [phenol] = 200 mg/L		Fe(III): 2.60 mg/L, Cu^{2+}: 7.76 mg/L	Good performance in the subsequent 3-cycle runs.	4–7	(Xia et al., 2011)
FeO_x/NiO_y/SBA-15	Acid Red 73	10 mmol/L	T = 25 ℃, $pH_0 = 3$, [Catalyst] = 0.6 g/L, [Acid Red 73] = 50 mg/L	99.3 (60 min)		Show high catalytic activity after 7 consecutive runs.		(Li et al., 2015a)
Cu/Fe/SBA-15	DPD	8 mmol/L	T = 25 ℃, $pH_0 = 4$, [Catalyst] = 10 mg, [DPD] = 100 mg/L	83 (120 min)	Cu < 0.5 ppm, Fe < 0.2 ppm	Catalytic performance almost unchanged after 3 recycles.		(Karthikeyan et al., 2016)
$Ce_{5\%}CuOy$	FLC	50 mmol/L	T = 25 ℃, $pH_0 = 5$, [Catalyst] = 0.1 g/L, [FLC] = 20 mg/L	94 (60 min)		No significant reactivity loss after 4 cycles.	3–9	(Zhang et al., 2020b)
CuO/CeO_2	Diclofenac	200 mg/L	$pH_0 = 5$, [Catalyst] = 1.2 g/L, [Diclofenac] = 20 mg/L	81.05 (60 min)	Ce: < 0.05 mg/L, Cu: 1.7 mg/L	Good performance in the subsequent 3-cycle runs.		(Zhu et al., 2019)
Cu/MnO_2	BZA	10.0 mmol/L	T = 24 ℃, $pH_0 = 7.13$, [Catalyst] = 1.0 g/L, [BZA] = 0.05 mmol/L	89 (60 min)	Mn: 0.198 mg/L, Cu: 0.077 mg/L	Catalytic activity decreased after 3rd and 5th runs.	3.40–8.23	(Zhang et al., 2016b)

generally exhibit higher catalytic activity and pH tolerance than the corresponding single metal oxides due to synergies and not just additive effects of two metal ions. More recently, Wang et al. (2018a, 2018b, 2018c) synthesized magnetic $MnFe_2O_4$ particles by sol-gel method. The obtained $MnFe_2O_4$ particles were found to more effectively activate H_2O_2 to remove norfloxacin (NOR) at near neutral conditions, and they could hold efficient catalytic activity at pH values of 6.6–8.0. Similarly, since the reaction between Fe(II) and Mn(III) was thermodynamically favorable, the electron transfer during the reaction was accelerated, which broken the limitation of relying on H_2O_2 for the conversion of Mn (III) to Mn(II). The reaction process was described as follows (Eq. (1), Eq. (4), and Eqs. (6)–(8)):

$$Mn(II)+H_2O_2 \rightarrow Mn(III)+H^{+}+\bullet OH \tag{6}$$

$$Mn(III)+H_2O_2 \rightarrow Mn(II)+OH^{-}+\bullet OOH \tag{7}$$

$$Mn(III)+Fe(II) \rightarrow Mn(II)+Fe(III) \tag{8}$$

Based on the above analysis, it could be inferred that the Mn ion in $MnFe_2O_4$ was essential for the efficient degradation of NOR. On the one hand, the reaction of Mn(II) and H_2O_2 contributed to the generation of •OH, and thus led to remarkable higher NOR removal efficiency (Tan et al., 2017). On the other hand, the •OH used for NOR degradation could also be generated by the redox cycles of Mn(III)/Mn(II), Fe(III)/Fe (II) interact with H_2O_2 synergistically. Moreover, Mn(III) reacted with Fe(II), to favor the reduction of Fe(III).

In general, the Fe-based bimetallic catalysts discussed above had metal active sites that would reduce Fe(III) to Fe(II), including Cu(I)/Cu (II) and Mn(II)/ Mn(III). This was consistent with previous reports that Cu(I)/Cu(II) (0.15 V) and Mn(II)/Mn(III) (1.51 V) thermodynamically beneficially reduce Fe(III) to Fe(II) (0.77 V) (Zhou et al., 2016). Their reducing metal sites played a vital role in improving the utilization of H_2O_2 and the removal rate of contaminants in Fenton-like systems. The introduction of another metal into Fe oxide provided a new method to improve heterogeneous catalytic activity (Cao et al., 2016). In particular, the metallic active sites formed by incorporating or doping new metals promoted the reduction of Fe(III) and facilitated the surface Fe cycle, leading to the accelerated H_2O_2 activation and reactive species generation.

3.2. *Go with oxygen vacancies (OVs)*

It has been proved that the formation of OVs can improve the utilization rate of H_2O_2 and significantly promote the formation of •OH (Jin et al., 2017). The introduction of OVs by incorporating or doping another metal greatly improves the catalytic performance due to their structural distortions. In addition, the excellent catalytic activity in Fenton-like reactions was also attributed to the synergistic effect of Fe and other transition metals in reducing Fe(III) and generating •OH. This point will be discussed in detail subsequently.

Different from the traditional heterogeneous Fenton-like reaction mechanism, OVs can extend the O−O bond of H_2O_2 to produce •OH and change the electronic structure, as well as chemical properties of Fe-based bimetallic oxides. Then, the interfacial electron transfer rate and the number of active oxidation species (such as •OH and $O_2•^-$) can be greatly increased. In some cases, for instance, Jin et al. (2017) found that it was the OVs formed by Cu replacing Fe in situ instead of accelerating Fe(III)/Fe(II) cycle that induced positive effects on the catalytic activity of Cu doped Fe_3O_4@FeOOH. Some other researchers have pointed out that surface OVs could act as active sites for H_2O_2 decomposition and •OH generation (Li et al., 2017a, 2017b, 2017c; Senthil et al., 2010; Wang et al., 2012). Besides, the local electron donor of OVs could directly promote the decomposition of the adsorbed H_2O_2 by means of Fenton reaction (Li et al., 2017a, 2017b, 2017c). According to Gao et al. (2019), an effective OVs-promoted Fe_2O_3-CeO_2 catalyst was synthesized and applied to degrade sulfamerazine (SMR). They revealed that the abundant OVs on catalyst surface significantly accelerated electron transfer and promoted the activation of H_2O_2, thus promoting the generation of •OH. Moreover, another active oxidizing species $O_2•^-$/$HO_2•^-$ formed by oxygen molecules adsorbed on OVs was very critical for promoting the redox cycle of Fe(II)/Fe(III). As shown in Fig. 2, the high activity OVs could be generated by other metals with lower oxidation state in situ replacing the skeleton Fe ions. Then, in the presence of OVs, the electronic structure of bimetallic oxides changed, which was probably due to the electron transfer from OVs to the surface Fe and O atoms. In the first step, OVs promoted the transfer of electrons from bimetallic oxide to adsorbed H_2O_2 (Wang et al., 2012). Next, due to moderate OVs, the extended O−O bond more easily activated H_2O_2 and decomposed it into •OH and $O_2•^-$ (Senthil et al., 2010). Besides, OVs was considered to be an active site that was not significantly influenced by the pH value of solution (Li et al., 2017a, 2017b, 2017c; Lu et al., 2011).

Accordingly, a method of activating H_2O_2 with different perovskite-type mixed metal oxides has been developed to eliminate organic contaminants owing to the high oxygen mobility and the stability of abnormal oxidation state of perovskite-type mixed metal oxides. The superior Fenton-like catalytic performance of perovskite-type mixed metal oxides probably caused by the comprehensive influence of several factors: the structure-enhanced effect, more active sites for H_2O_2 activation, and accelerated electron transfer. As we all know, the general element composition of perovskite-type oxides is ABO_3, in which A is a rare earth metal and B is transition metal (Arandiyan et al., 2013). So far, a number of studies have documented that many perovskites mixed metal oxides were effective in oxidizing and removing a host of organic compounds by changing the A and B sites in ABO_3 (Luo et al., 2010; Rusevova et al., 2014; Sannino et al., 2013; Wang et al., 2011). It has been demonstrated that excellent adsorption capacity is highly beneficial for high catalytic property (Liu et al., 2020a). In a representative work, Leiw and co-workers (Leiw et al., 2013) discovered that high concentration organic contaminants could be efficiently degraded by metal oxide strontium ferrite $SrFeO_3$ (SFO). This was resulted from the enhanced adsorption of anionic contaminants on the surface of ball-milled SFO metal oxides with positive charges (Leiw et al., 2013). To further illustrate, Nie and colleagues (Nie et al., 2015) proposed a reaction mechanism based on the surface interaction of $LaFeO_3$ and H_2O_2. The possible mechanism was displayed in Fig. 3. Firstly, H_2O_2 was chemically adsorbed on the surface of $LaFeO_3$ to form $LaFeO_3$-H_2O_2 surface complex, which was the main reason for pollutant degradation. Secondly, it changed the chemical environment of Fe in $LaFeO_3$ (Sun and Pignatello, 1992), and significantly weakened the O-O bond in H_2O_2 (Luo et al., 2010; Strathmann and Stone, 2002). Then, through the surface OVs mechanism, the Fe(III)/Fe(II) cycle was accelerated, and more active oxygen species such as •OH and $O_2•^-$/$HO_2•^-$ were generated and have been proved to be directly involved in this reaction. To further explain the formation mechanism of active substances, Chong's group (Chong et al., 2017) reported the synthesis of $FeCeO_x$ and its application as an efficient Fenton-like catalyst to degrade diclofenac. It has been confirmed that the existence of surface Ce and Fe sites and abundant OVs were mainly responsible for H_2O_2 dissociation and active species generation. As shown in Fig. 4, OVs on the surface of metal oxides catalyzed the dissociation of H_2O_2 to generate $^1O_2$. The results identified the $^1O_2$ as the main active species in the heterogeneous Fenton-like system, and $O_2•^-$ also participated in the degradation process of diclofenac. Among them, $O_2•^-$ could be formed by transferring electrons to molecular oxygen. The results indicated that Fe (II), Fe (III), Ce (III) and Ce (IV) coexisted on the $FeCeO_x$ surface and accepted the electron from OVs, which was beneficial to the decomposition of H_2O_2 and the formation of $^1O_2$ during the reaction (Chong et al., 2017).

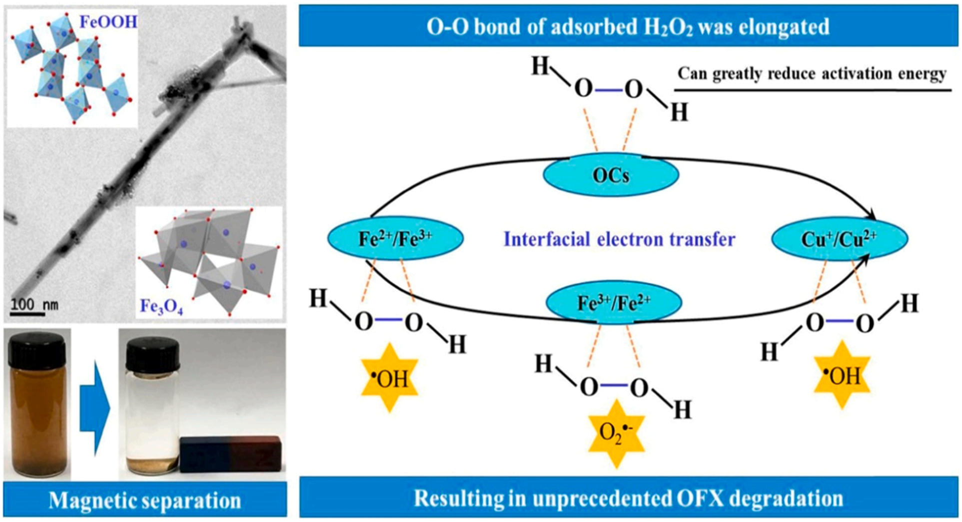

Fig. 2. Proposed OVs involved heterogeneous Fenton-like reaction mechanism of Cu doped Fe_3O_4@FeOOH. Reproduced from Ref. (Jin et al., 2017), Copyright 2017 American Chemical Society.

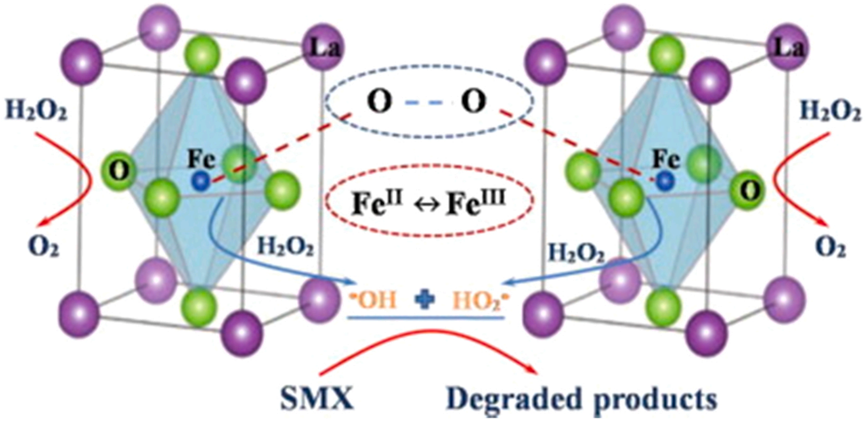

Fig. 3. Enhanced Fenton-like degradation of refractory organic compounds by surface complex formation of $LaFeO_3$ and H_2O_2. Reproduced from Ref. (Nie et al., 2015), Copyright 2015 Elsevier B.V.

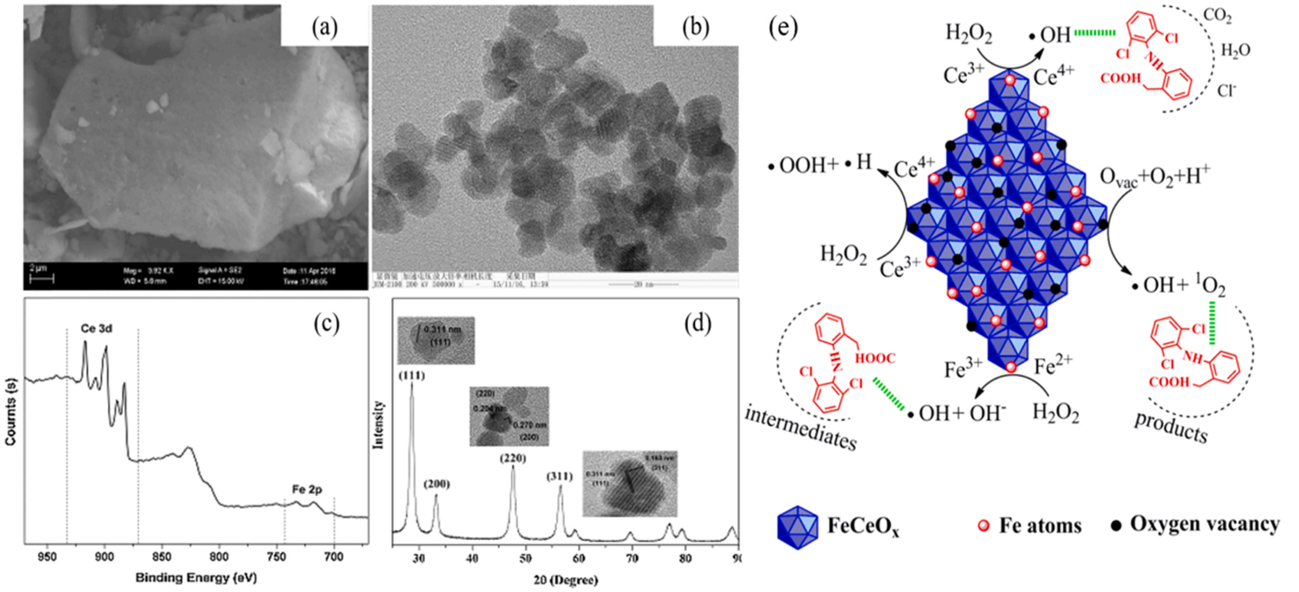

Fig. 4. Characterization of $FeCeO_x$ (a) SEM, (b) HRTEM, (c) XPS, (d) XRD and (e) Schematic diagram of diclofenac reaction mechanism in FeCeOx-H_2O_2 Fenton-like process. Reproduced from Ref. (Chong et al., 2017), Copyright 2017 Elsevier B.V.

3.3. *Carry out structural advantages*

The introduction of transition metal ions usually leads to significant changes in the properties of Fe-based bimetallic catalysts, such as surface area, stability, pH tolerance, and catalytic activity (Wang and Tang, 2021b). The Fenton-like reaction catalyzed by this new type of bimetallic oxide has superior catalytic activity. One reason is that the larger specific surface area brings about an increase in accessible active sites. The oxygen-containing functional groups on the surface are favorable for adsorption, and the pore structure is conducive to mass transfer, which has a positive impact on the degradation performance of target contaminants.

Considerable evidences showed that bimetallic composites could optimize various surface properties of catalysts, such as specific surface, surface defect content and electronic structure (Eshaq et al., 2020; Li et al., 2018). These improvements could be attributed to: (i) the introduction of foreign metals may make the catalyst surface coarser and increase the surface area; (ii) the number of active sites on catalyst surface increased significantly by introducing other transition metals; and (iii) the positive synergistic effect between different metals was beneficial to accelerate the electron transfer and redox cycle of metal ions (Hammouda et al., 2017; Sun et al., 2019; Zhang et al., 2016a,b).

Following the similar idea, magnetic nanoparticles bimetallic oxides have been extensively studied, mainly because they had a series of advantages such as large specific surface area, high surface activity, excellent durability and reusability (Hu et al., 2011; Luo et al., 2010). When magnetic nano bimetallic oxide composites are utilized in heterogeneous Fenton-like catalysis, their nanostructures and magnetism usually contribute unique collective and synergistic catalytic performance for contaminants removal, and exhibit prominent physical and chemical properties in degradation processes, such as good recyclability, easy recovery, high stability and dispersion. On the one hand, reducing the particle size to nanoscale can significantly increase the specific surface and the number of active sites of the catalyst, and thus lead to higher catalytic activity (Huang et al., 2005). On the other hand, the composite material can be easily separated from treated water and reused by applying a magnetic field, which is a particularly significant advantage for magnetic nanoparticles. Encouraged by the advantages of magnetic nanocomposite materials, Xu and Wang (2012) prepared a magnetic nano-scaled Fe_3O_4/CeO_2 composite, which catalyzed H_2O_2 to degrade 4-chlorophenol (4-CP). The results suggested that the synergistic effect among CeO_2 and Fe_3O_4 was the main reason for the high catalytic activity of the composites (Fig. 5) (Xu and Wang, 2012). Besides, its superior activity could be attributed to the fact that CeO_2 promoted the dissolution of Fe_3O_4, increased the relative mass transfer rate and chemical reaction rate of reaction sites, thus improving the removal rate of 4-CP. This observation was not limited to magnetic nano-bimetallic oxides and other Fenton-like catalysts have been described previously. Including Fe_3O_4/CeO_2 nanoparticles (Xu and Wang, 2012), the preparation of Fe-based catalysts with core/shell structure and their application in wastewater treatment in heterogeneous Fenton-like processes are promising (Bunker and Karnes, 2004; Xu et al., 2007). Fe-based catalysts with core/shell structure, that is, the core is composed of magnetic materials and the shell consists of active metal oxides or composite oxides, tend to exhibit excellent catalytic performance.

In 2011, an efficient Fenton-like catalyst, namely Fe core/shell $Fe_3O_4/FeMnO_x$, has been synthesized by Xing's group (Xing et al., 2011). Different from the additive effect of simple mixing of core/shell structure and magnetic nanomaterials, $Fe_3O_4/FeMnO_x$ exhibited surprising and unique properties. The researchers noted that changes in surface properties were related to the structural characteristics of the solid catalyst, such as pore size and specific surface, which affected whole catalytic process and determined final catalytic efficiency. It was also found that $Fe_3O_4/FeMnO_x$ exhibited higher catalytic activity for contaminants removal due to the presence of more •OH on the surface of $Fe_3O_4/FeMnO_x$ (Xing et al., 2008; Zhang et al., 2008). In addition, the superior performance of $Fe_3O_4/FeMnO_x$ was attributed to the structural enhancement effect of core/shell structure, which accelerated electron transfer and had more active centers than a single magnetic core. In a more recent report, Huang's group (Huang et al., 2017a, 2017b) synthesized a new $Mn_{1.8}Fe_{1.2}O_4$ nanosphere and applied it to degrade BPA. It was concluded that $Mn_{1.8}Fe_{1.2}O_4$ nanospheres showed much better performance than Mn/Fe single metal oxides over a wide pH range of 4–10. Since the contact between Mn and Fe was sufficiently effective, the degradation reaction could proceed effectively. Moreover, in this work, solid Mn and Fe acted as active sites and adsorption sites respectively, and the combination of the two components presented a positive synergistic effect (Huang et al., 2017a, 2017b). Therefore, the unique structure of $Mn_{1.8}Fe_{1.2}O_4$ nanospheres allowed diffusion of reactants to active sites, accelerating the surface redox process, thereby improving the degradation activity of BPA.

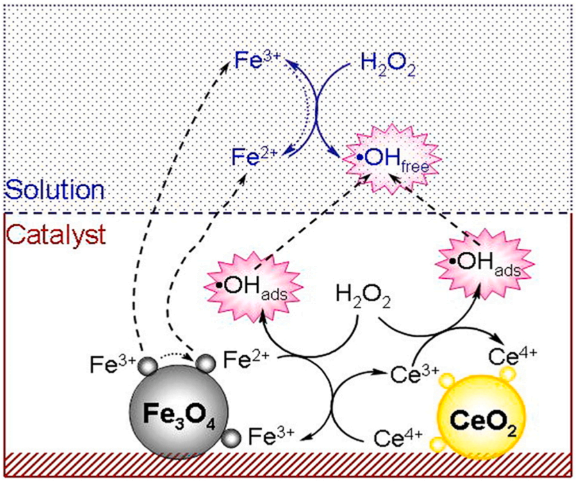

Fig. 5. Schematic diagram of the reaction mechanism of the H_2O_2 activation by Fe_3O_4/CeO_2 catalyst under acidic condition. Reproduced from Ref. (Xu and Wang, 2012), Copyright 2012 American Chemical Society.

3.4. Join forces with the support

In heterogeneous Fenton-like process, Fe ions are easily aggregate and leach, which inevitably leads to the loss of Fe-based catalysts and reduces its practical performance. To solve these problems, the immobilization of Fe-based bimetallic oxide on the support is considered to be a useful method. In the supported bimetallic oxides catalysts, since the metal particles loaded on the supports showed better uniformity, narrow distribution and smaller particle size, and are more accessible to the reactants, they exhibit a less tendency to leach metal ions. In addition, loading the bimetallic oxides on suitable support materials can further improve the physical and chemical properties of bimetallic oxide composites (Karthikeyan et al., 2016; Li et al., 2015a; Xia et al., 2011). It is noteworthy that the existence of support materials not only accelerates the electron transfer between Fe(II)/Fe(III) redox pairs, but also improves the adsorption of contaminants and promotes the exposure of surface-active sites.

Up to now, multiple types of Fe-based bimetallic oxides complexes have been developed by using diverse porous materials (Li et al., 2015b; Navalon et al., 2010; Rache et al., 2014; Wang et al., 2015; Xia et al., 2011). Typically, Santa Barbara Amorphous-15 (SBA-15) was considered to be a promising porous support. This is mainly because it has a series of advantages such as large specific surface, ordered channels and poles, tunable pore size, narrow pore size distribution and high hydrothermal stability (Li et al., 2015b; Navalon et al., 2010; Zhao et al., 1998). Besides, recent progress has shown that the catalyst obtained by adding Fe-based bimetallic oxides into the space-limited porous material not only has higher catalytic activity nanoparticles (because of the confinement effect and size effect) (Cai et al., 2013; Cargnello et al., 2013; Li et al., 2015b; Rossy et al., 2013), but also the density of local active sites increases in a narrow space (Cui et al., 2013; Yu and He, 2012). What is even more interesting is that the tendency of nanoparticles shedding is greatly reduced due to the strong interaction between porous material surface and active ingredients (Ungureanu et al., 2013). As reported by Li and co-workers (Li et al., 2015a), a magnetic Ni-Fe Fenton-like catalyst (FeO_x/NiO_y/SBA-15) was successfully synthesized using mesoporous material SBA-15 as a support. The catalyst exhibited high dye (Acid Red 73) removal efficiency with negligible Fe leaching. The total H_2O_2 utilization efficiency after seven cycles was more than 95%, revealing that its stability and activity were higher than most reported Fe-based bimetallic oxides (Wang et al., 2018a, 2018c, 2018b; Xing et al., 2011; Zhang et al., 2020b). In addition, the support can affect the catalytic performance of Fe-based bimetallic oxide complexes by influencing the spatial structure and the metal carrier interaction between the SBA-15 surface and the Ni species (host), so as to stabilize Ni species and form spherical or ellipsoidal Ni nanoparticles. It can be clearly seen from Fig. 6 that Ni and Fe were evenly distributed on the surface of FeO_x/NiO_y/SBA-15. The presence of Ni(0) facilitated the reduction of Fe(III) in Fenton-like reaction (Eq. (5)). Besides, the reaction activity of Ni species with H_2O_2 was low, thereby prolonging the lifetime of adsorbed H_2O_2, and ultimately promoting the utilization of H_2O_2, and increasing the production of oxidant (Jiang et al., 2008; Li et al., 2015a). It could be observed in this study, Fenton-like reaction occurred sequentially or/and simultaneously between mixed oxides. These oxides cooperated seamlessly on the nanoscale, and the reactions are as follow (Eq. (1) and Eq. (5) and Eq. (9)):

$$\mathrm{Ni(II)+H_2O_2 \rightarrow Ni(III)+OH^- + \bullet OH} \quad (9)$$

In addition to the molecular sieves discussed above, other common supports such as Al_2O_3 and carbon materials (CMs), have proven to be effective supports for coupling with Fe-based catalysts to improve their Fenton-like catalytic activity (Tang and Wang, 2019). Among them, CMs including activated carbon fiber (ACFs), activated carbon (AC), carbon nanotubes (CNTs), graphene (GO), carbon aerogel (CA) or xerogels (CX), are widely used as supports for Fenton-like catalysts (Wang et al., 2017,

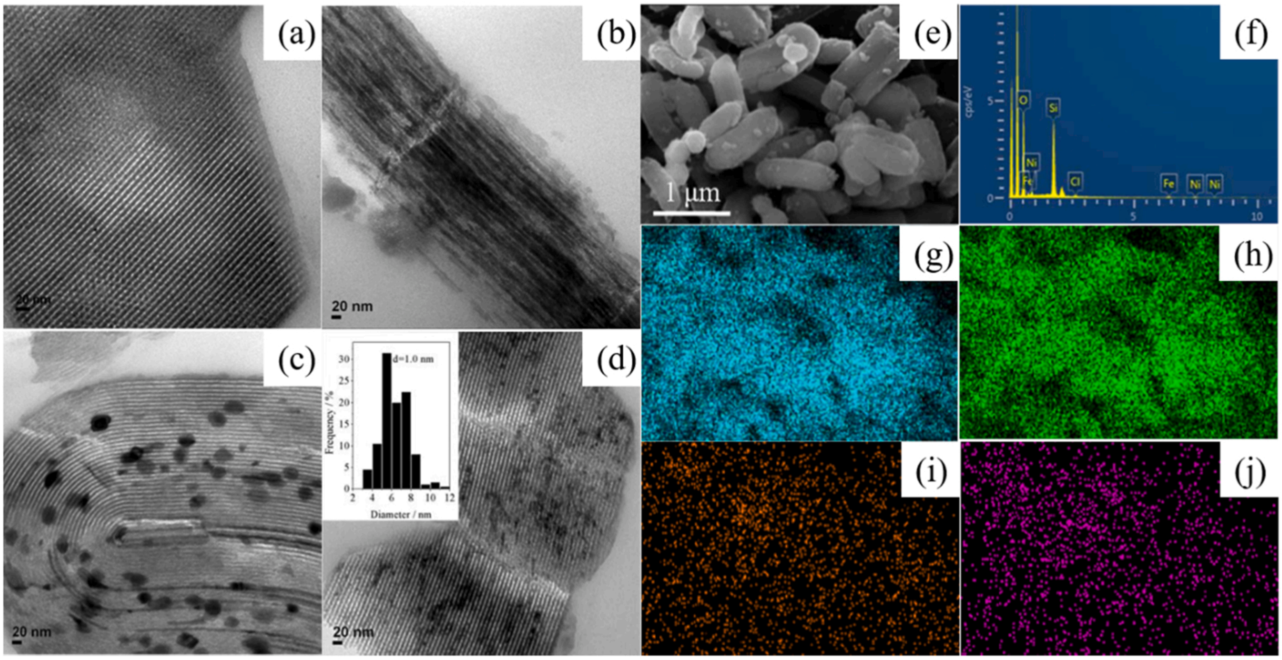

Fig. 6. TEM images of the following samples: (a) pure SBA-15, (b) FeO_x/SBA-15, (c) NiO_y/SBA-15 and (d) FeO_x/NiO_y/SBA-15, and (e) SEM photograph, (f) elemental mapping images of FeO_x/NiO_y/SBA-15, and (g) Si, (h) O, (i) Fe (j) Ni with color superposition. Reproduced from Ref. (Li et al., 2015a), Copyright 2015 Elsevier B.V.

2015). It has been elucidated that some CMs themselves can directly activate H_2O_2 to produce •OH (Liu et al., 2018b; Ribeiro et al., 2016). In addition, CMs tend to have electronic and conductive properties, large surface area and a highly open pore structure (Liu et al., 2020a). These excellent properties not only allow bimetallic Fenton-like catalysts to be well dispersed on their surfaces, but also promote the continuous formation of •OH, thereby improving degradation efficiency (Zuo et al., 2021). For example, in 2017, Fe-Cu bimetallic nanoparticles supported on carbon nanofibers (FeCu/CNF) was prepared by Wang et al. (2017) as a Fenton-like catalyst, which showed efficient removal of Acid Orange II (AOII). Besides, Al_2O_3 is also a promising support for Fenton-like catalysts. Al_2O_3 is suitable as a catalyst support because of its excellent chemical stability, large specific surface area, and high thermal stability (Yang et al., 2008). In a related work, Wu et al. (2019) used $LaFeO_3$ as a Fenton-like catalyst to investigate the effects of different supports on the removal of Acid Orange 7 (AO7). The results showed that Al_2O_3 as the $LaFeO_3$ support exhibited the best •OH generating capacity and catalytic activity among the investigated $LaFeO_3$ catalysts, primarily because of its abundant chemisorption surface active oxygen, suitable redox performance and fast electron transfer.

In some cases, there may be a synergistic effect or interaction between the support material and the catalyst particles, thus showing unique performance, which has a positive impact on catalytic properties. The development of effective Fe oxide complexes by loading Fe oxides on suitable support materials has been well-documented. In a representative work, Li and colleagues (Li et al., 2020) fabricated a porous structure (Fe_3O_4-Cs) Fenton-like catalyst and studied its application in the degradation of tetracycline (TC) for the first time. As depicted in Fig. 7, Fe_3O_4-Cs had a stable porous structure and abundant active centers, which account for the excellent catalytic activity.

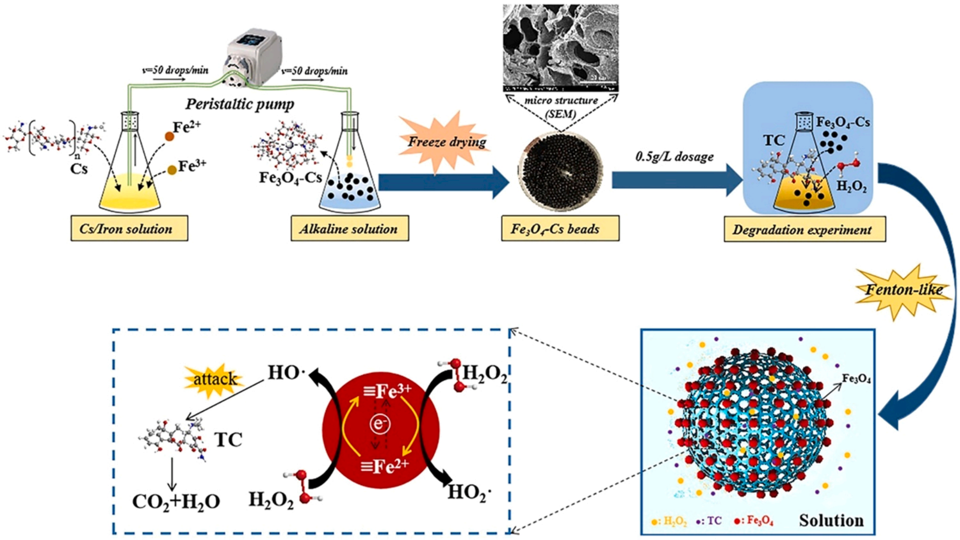

Fig. 7. Schematic illustration showing the main steps of H_2O_2 activation and TC degradation in the Fe_3O_4-Cs/H_2O_2 Fenton-like system. Reproduced from Ref. (Li et al., 2020), Copyright 2019 Elsevier B.V.

Besides, a possible synergy between the two components was believed to promote the formation of •OH for TC degradation. Similar observations were reported for the synergy between other porous materials and Fe-based bimetallic oxides in the Fenton-like process. At present, MCM-41 is also considered as an ideal support for well-designed Fenton-like catalysts. It is a new type of nanostructured material with the pores in an orderly hexagonal shape, uniform size, continuous adjustment of the pore diameter in the range of 2–10 nm, and large specific surface area. More importantly, the Al in MCM-41, as an electron donor, plays a vital role in increasing the electron density near active metal center, which greatly boosts the adsorption of H_2O_2 and accelerates the reaction. In addition, the increased surface acidic oxygen-containing groups by Al and the H^+ concentration area on catalyst surface greatly facilitate the conversion of H_2O_2 to highly active species instead of being decomposed into H_2O and oxygen, thereby significantly improving the catalytic performance (Lee et al., 2005; Xia et al., 2011). In a related report, Xia et al. (2011) described the application of MCM-41 containing Al as a support of Fe-Cu bimetallic oxides. As expected, Fe/Cu/MCM-41 showed better phenol degradation efficiency in the presence of H_2O_2. The results suggested that the superior adsorption performance of MCM-41 led to a better catalytic activity of Fe/Cu/MCM-41, and the combination of effective adsorption and oxidation helped Fe/Cu/MCM-41 to remove phenol efficiently. They also indicated that the synergistic effect of surface acid groups and the increase of electron density around the active metal center were responsible for the improved catalytic activity of Fe/Cu/MCM-41.

To date, various types of Fe-based bimetallic oxides (or Fe-based bimetallic oxide complexes) have been designed and fabricated. In general, their Fenton-like properties are better than conventional Fe oxides. The excellent Fenton-like degradation performance is mainly attributed to the tacit coordination of two different transition metal oxides. First, the doping of other metals allows rapid electron transfer and redox cycling. Second, the introduction of OVs by incorporating or doping the second metal greatly promotes the utilization of H_2O_2 and the formation of •OH. In addition, the large specific surface and stable porous structure can offer abundant adsorption sites for target contaminants by adding active ingredients to porous materials in a limited space. These properties work synergistically, resulting in a significant enhancement of Fenton-like activity.

4. Fe-free bimetallic catalyst for heterogeneous Fenton-like reaction

As aforementioned, numerous reports have focused on Fe-based bimetallic catalysts composed of Cu, Mn, and Fe, which has also attracted attention in the field of Fe-free transition metals interactions. Apart from the widely reported Fe-based bimetallic catalysts, Fe-free bimetallic oxides (such as Cu-Mn bimetallic oxides) have been proved to be another emerging class of catalysts that can also act as heterogeneous Fenton-like catalysts and effectively remove target contaminants. Some heterogeneous Fenton-like processes for removing organic compounds in wastewater by Fe-free bimetallic oxides (or Fe-free bimetallic oxide complexes) are presented in Table 1. These records clearly showed that the synergistic effects between different metal oxides were very conducive to Fenton-like degradation of recalcitrant organic contaminants with short treatment times. Despite Fe-free bimetallic catalysts have achieved high performance, the actual role of each metal in catalysis is still unclear, hindering the further development of Fe-free catalysts. Thus, summarizing the latest progress in this field is very key to the design of Fe-free bimetallic catalysts with higher performance.

Many transition metal elements (e.g., Cr, Ce, Cu, Co, Mn), have been frequently used as the alternative of Fe in Fenton-like processes (Karthikeyan et al., 2016; Wang et al., 2018). These metals can cyclically catalyze H_2O_2 to produce •OH through the conversion between their different valence states, which behave similarly to Fe in the Fenton-like reaction. In fact, a large number of reports have studied the application of Fe-free catalysts in Fenton-like, especially Cu (Zhu et al., 2019), Mn (Zhang et al., 2016a, 2016b) and Ce (Wen et al., 2015) to expand the pH range of Fenton-like reactions. Catalysts containing Cu have attracted much attention because of the similar redox properties of Cu(II)/Cu(I) to Fe(III)/Fe(II) and a wide range of pH values (Peng et al., 2019). Besides, Cu is the richest and cheapest transition metal element. Consequently, Cu-based materials as heterogeneous Fenton-like catalysts have great potential in environmental applications. Although extensive works have confirmed that Cu- containing catalysts exhibited high catalytic activity in Fenton-like systems, there is still room to improve their degradation efficiency (Xiang et al., 2019). Designing Cu-based catalysts with better surface properties is a remarkable route to give full play to their potential in Fenton-like systems (Wang et al., 2018a, 2018b, 2018c). A variety of surface properties such as specific surface area, electronic structure and surface defect content of the catalyst obtained by introducing foreign metals into Cu-based materials have been optimized (Eshaq et al., 2020). At the same time, the synergistic effect between different metals is conducive to accelerating the electron transfer and redox cycle of metal ions (Ben Hammouda et al., 2017).

In addition to Cu, Ce can also be utilized for the synthesis of bimetallic oxides catalysts. On the one hand, the redox cycle of Ce between +3 and +4 oxidation states leads to its high oxygen storage capacity (Campbell and Peden, 2005). On the other hand, in the presence of H_2O_2, the behavior of Ce as a rare earth element is similar to that of Fe in Fenton-like reaction (Heckert et al., 2008). In a recent work, a new Cu-Ce bimetallic catalyst was proposed by Zhang and co-workers (Zhang et al., 2020b). The degradation experiments showed that it presented higher reaction activity, wider pH applicability and better reusability for the degradation of fluconazole (FLC) than single metal Cu compounds. The results also indicated that the introduction of Vanadium (V) into Cu-based materials could improve the surface performances of Cu catalysts, such as adsorption capacity, surface defects and active site concentration, which were closely related to the catalytic activity (Zhang et al., 2020b). These findings are consistent with the conclusions drawn in many other reports. According to Zhang et al. (2020), there were electron-rich centers and surface OVs around the Cu/V active site, which facilitated the catalytic activity, and led to the rapid dissociation of FLC (Zhang et al., 2020a).

In order to further improve the catalytic performance of Fe-free bimetallic oxide, the immobilization of Fe-free bimetallic oxide on the support materials was later designed (Xia et al., 2011; Zhang et al., 2016). The addition of support allows Fe-free bimetallic oxides uniformly distributed on the surface, reduces the leaching of metal ions, and improves the accessibility of the active components to reactants (Du et al., 2016). In addition, due to the accelerated electron transfer ability brought by support, Fe-free bimetallic oxide complexes show better Fenton-like activities than unsupported Fe-free bimetallic oxides in the degradation of contaminants. Till now, a variety of metal oxides (such as CeO_2, Al_2O_3), zeolites, clays and carbon materials have been used as supports for Fenton-like catalysts (Rao et al., 2018; Xu et al., 2018). In particular, CeO_2 is considered to be a promising support due to its abundant OVs defects, Ce(IV)/Ce(III) redox pairs (Chong et al., 2016) and enhanced catalytic properties when it forms bimetallic oxides (Gupta and Garg, 2017; Li et al., 2017a, 2017b, 2017c; Yadav and Garg, 2012; Zhou et al., 2018). For instance, a high-efficiency catalyst CuO/CeO_2 was fabricated using a ultrasonic impregnation method to degrade diclofenac in water (Zhu et al., 2019). The results showed that the degradation efficiency of diclofenac in $CuO/CeO_2/H_2O_2$ system was higher than that in the CuO/H_2O_2 system and CeO_2/H_2O_2 systems, indicating that there was a synergy between CuO and CeO_2. Further studies have shown that the synergy between CuO and CeO_2 may be attributed to two factors. Firstly, Cu was loaded in CeO_2 to increase OVs and improve the catalytic property of CuO/CeO_2. Secondly, there was an electronic interaction between the metal and the carrier, which led to a promoted redox effect between Cu(II)/Cu(I) and Ce(IV)/Ce(III), thus facilitating the reduction of CuO (Konsolakis, 2016). Based on the above findings, the potential mechanism of Fenton-like reaction in CuO/-CeO_2/H_2O_2 system was presented in Fig. 8. Firstly, H_2O_2 was converted to •OH by CuO. More importantly, Ce(III) and H_2O_2 also generated •OH by splitting the O-O bond of H_2O_2. After that, the synergistic effect between Cu and Ce (Eq. (10)) facilitated the redox cycle of Cu(II)/Cu(I) and further promoted the generation of •OH. The results also showed that CuO/CeO_2 had a larger specific surface, higher porosity and excellent element dispersion, allowing rapid electron transfer and improving the catalytic performance (Prathap et al., 2012).

$$Cu(II)+Ce(III)\rightarrow Cu(I)+Ce(IV) \tag{10}$$

Similarly, Zhang and co-workers (Zhang et al., 2020b) developed another application of Cu-Ce bimetallic catalyst in aqueous medium. The as-fabricated $Ce_{5\%}CuO_y$ exhibited high catalytic activity within a wide range of PH values (3–9), and 94% of FLC was removed, which was much higher than the removal efficiency of CuO_y. This study suggested that the significant synergistic effect between Cu and Ce had a positive impact on the degradation performance of $Ce_{5\%}CuO_y$. In addition, the introduction of Ce increased Cu(I) sites and unpaired electrons, which improved the degradation efficiency. A reasonable mechanism could explain this significantly enhanced FLC degradation performance (Fig. 9). Firstly, Cu(I) was the main active site for triggering the heterogeneous Fenton reaction. Secondly, the coexistence of Cu (including Cu(II), Cu(I), Cu(0)) on the surface could promote the decomposition of H_2O_2 and generate reactive oxygen species (Zhang et al., 2020a). In addition, Ce doping increased the specific surface and pore volume of the material, improved the surface roughness of the composite material, and facilitated the electronic interaction between Cu and Ce, thereby improving the redox properties of bimetallic catalyst (Li et al., 2018a, 2018b, 2018c; Lykaki et al., 2018). There were a large number of unpaired electrons in OVs, which led to a quantity of electron-rich centers on catalyst surface. The H_2O_2 adsorbed on the active center first formed a structure that was easier to decompose, and then received electrons from neighboring Cu(I) and quickly decomposed into •OH (Jin et al., 2017; Wang et al., 2018).

After this study, extensive attempts have been made, such as continuously doping Cu and other metal elements to prepare new types of bimetallic oxides and their complexes. Especially Mn oxide has received significant attention, which was attributed to its low cost and high stability (Ghuge and Saroha, 2018). Recently, Mn oxides and the ones adding transitional metals are widely used to trigger Fenton-like reactions (Zhang et al., 2016a, 2016b). In Fenton-like reactions, the Mn(III)/Mn(II) redox cycle (1.51 V) is thermodynamically feasible. For instance, Zhang and colleagues (Zhang et al., 2016a, 2016b) reported the discovery of Cu/MnO_2 catalyst, which exhibited better adsorption and catalytic activity than pure Mn oxide or Cu oxide in Fenton reaction. This increase may be due to the following factors: (i) the incorporation of Cu increased the OVs, resulting in an increase in the density of surface •OH, which were conventional reaction sites for surface adsorption (Pham et al., 2016) and catalytic oxidation (Lyu et al., 2015); (ii) The introduction of Cu reduced the temperature of Mn reduction, accelerating mobility of lattice oxygen in MnO_2 and improving the reducibility of MnO_2. This would make the Mn component more active for catalytic oxidation (Zhang et al., 2016a, 2016b). Although the doping of Fe-free metals increases the specific surface area of Fe-free bimetallic catalysts, accelerates the reduction process of low-valent metals and achieves high catalytic activity. However, in order to commercialize non-ferrous bimetallic catalysts, more schemes need to be provided to construct Fe-free bimetallic catalysts with high stability.

The above analysis has confirmed that the reaction rate and mineralization of bimetallic oxide systems were significantly improved compared with Cu oxide alone. The continuous degradation experiments showed that the proposed bimetallic oxides and their complexes system had sustainability and high energy efficiency, ensuring its application in wastewater treatment. Meanwhile, authors attempted to experimentally verify the beneficial synergy between different non-Fe oxides in the process of contaminant removal. At this point, the enhanced catalytic activity was mainly attributed to the synergy between different oxides. Generally speaking, this process could improve the adsorption capacity of target pollutants, increase the concentration of free radicals and accelerate electron transfer. Consequently, compared with Fe-free metal oxides used in wastewater treatment, this synergistic process was more sustainable.

5. Reusability and suitable pH of bimetallic oxides and their complexes

From the perspective of actual applications, reusability is one of the most critical issues in heterogeneous Fenton-like processes (Zhuang and Wang, 2021). Almost all experiments, as summarized in Table 1, the fabricated bimetallic oxides and their complexes still exhibit high catalytic activity after three or more recycles, indicating that the Fenton-like process has little effect on the main structure of bimetallic oxides and their complexes (Karthikeyan et al., 2016; Zhang et al., 2016).

In order to better understand the concentration of leached metal ions, we compared the concentrations of bimetallic oxides and their complexes used in the experiment (in Table 1). As shown in Table 1, the concentrations of leached metal ions are very low (0.05–11.8 ppm). The result also showed that the leaching capacity of bimetallic Fenton-like catalysts is usually lower than that of traditional Fenton-like catalysts.

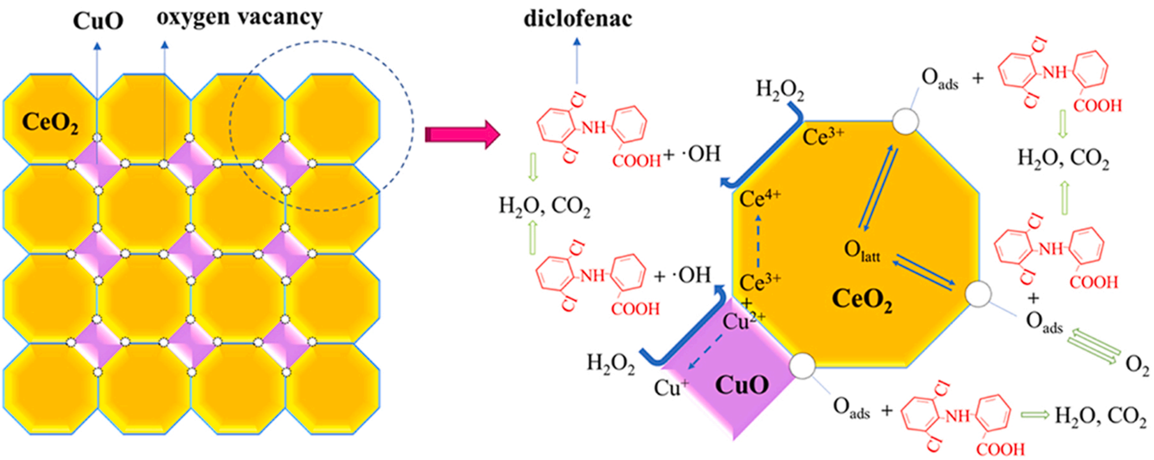

Fig. 8. Potential mechanisms of diclofenac degradation in CuO/CeO_2-H_2O_2 system. Reproduced from Ref. (Zhu et al., 2019), Copyright 2019 Frontiers in Chemistry.

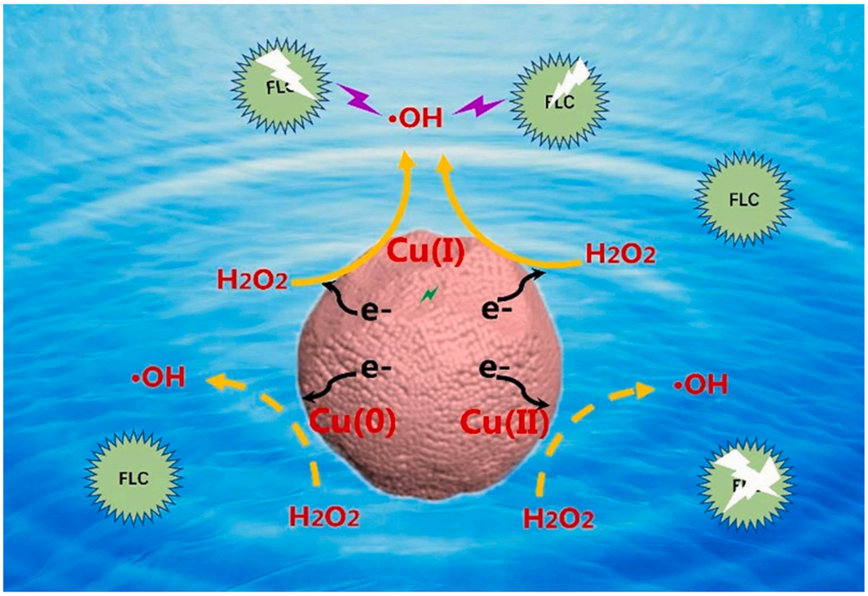

Fig. 9. Schematic presentation of FLC degradation mechanism involved in the Ce_xCuO_y/H_2O_2 system. Reproduced from Ref. (Zhang et al., 2020b), Copyright 2020 Elsevier B.V.

For example, Zhang's team (Zhang et al., 2014) found the Cu leached from Cu_2O after 120 min reaction was only 9% of $CuFeO_2$ catalyst.

It should be noted that only a few studies had looked at the potential catalytic activity of the solutions containing leached material (Luo et al., 2010; Xia et al., 2011; Zhang et al., 2014, 2016). These studies have compared the degradation efficiencies of pollutants by bimetallic oxides/complexes catalyzed Fenton-like process and the leached metal ion catalyzed homogeneous Fenton process. For example, Zhang et al. (2014) compared the degradation process of BPA catalyzed by $CuFeO_2$ and the homogeneous Fenton process catalyzed by leached Fe and/or Cu ions. The results have confirmed that under different pH conditions, the removal rate of BPA by the leaching solution (6%−14%) is much lower than that in the corresponding heterogeneous $CuFeO_2/H_2O_2$ system (95%−99.2%). It indicated that the degradation of BPA is mainly caused by the heterogeneous catalytic reaction on the surface of $CuFeO_2$. Researches also showed that when using the same catalyst concentration, the degradation ability of bimetallic oxides and their complexes catalyzed Fenton-like processes was comparable to (or even more effective than) that of homogeneous Fenton processes.

On the other hand, bimetallic oxides and their complexes generally show wider suitable pH than traditional Fenton-like catalysts (Xing et al., 2008; Zhang et al., 2020b). For example, Xing and his co-workers (Xing et al., 2008) reported that in the pH range of 3.5–9.0, Fe_3O_4/-$FeMnO_x$ exhibited high catalytic activity for MB removal. One possible explanation for this phenomenon is that the combination of two different transition metals makes it possible to carry out the Fenton-like process in a broader pH range. On the one hand, the presence of bimetallic makes metal leaching less and higher stability. On the other hand, the regeneration process of the low-valence metals is accelerated during bimetallic reaction, especially the resistance to the change of working pH was enhanced. A similar result has been reported in the subsequent work, as reported by Wan and Wang (2016), the obtained Fe_3O_4/Mn_3O_4-RGO showed excellent removal efficiency in the pH range of 3.0–7.0. Therefore, according to the data obtained from laboratory scale experiments (Table 1), it can be reasonably concluded that bimetallic oxides and their complexes are usually effective in a wide range of pH values (3.0–9.0).

6. Conclusions and prospects

In summary, this review summarized and exemplified the recent advances in the application of bimetallic oxides and their complexes in Fenton-like processes. The respective contributions of different components in each type of bimetallic oxides and their complexes catalysts were also discussed, and the synergistic mechanisms of the two metals were briefly introduced. Despite a very short history of the development of bimetallic oxides and their complexes, they have received considerable attention and achieved excellent results in recent years. The concept of constructing composite oxide catalysts from different types of metals offers several potential advantages over conventional single metal oxides catalysts. Well-designed bimetallic oxides and their complexes can take advantage of the advantages of both metal oxides while avoiding the shortcomings of each component. As a result, these bimetallic oxides and their complexes are capable of forming •OH from H_2O_2 in a wide pH range, and exhibit enhanced Fenton-like performance on pollutant degradation and H_2O_2 utilization with limited metal ion leaching and long-term stability. In particular, the addition or doping of new metals can perform one or more of the following functions: (i) coarsening the catalyst surface and increasing the surface area (Hammouda et al., 2017; Zhang et al., 2016); (ii) significantly increasing the number of active sites on the catalyst surface; and (iii) accelerating the electron transfer and redox cycling of metal ions (Hammouda et al., 2017). Thus, bimetallic oxides and their complexes usually exhibit significantly higher Fenton-like activity than that of single metal oxides. The synergistic effect between different metals in various bimetallic oxides and their complexes will provide unprecedented opportunities for the development of alternative Fenton-like catalysts.

Despite the steady improvement in the design and preparation of bimetallic oxides and their complexes catalysts and their applications in heterogeneous Fenton-like catalysis, there are still many challenges need to be addressed. A number of improvements worth further efforts are listed as follows:

(1) The key factor of Fenton-like reaction system is •OH, which is the main active substance and is essentially reactive and a short-lived oxide. Therefore, more in-depth studies are needed in the field of extending its life.

(2) Up to now, few studies have investigated economic costs. Since economic analysis is essential for the selection of abundant, low cost and continuously available catalysts, a great deal of effort is required to assess the cost. Besides, environmental risk assessment of these bimetallic oxides and their complexes should be carried out adequately before practical application.

(3) The mechanism of H_2O_2 activation to generate •OH has not been extensively reported in the literature so far, and there is no consensus on the reactions involved. More detailed investigations are still needed in further studies to understand the mechanisms and reactions of H_2O_2 catalyzing the decomposition of organic contaminants in Fenton-like processes.

(4) Future researches should focus on the development of new magnetic nano catalysts with higher reactivity and stability. At present, the known mechanisms are mostly empirical, and the deeper mechanisms related to synergistic effects of bimetallic oxides and their complexes catalysts need to be studied systematically.

(5) Then, most of the research in this field has been carried out through bench-scale experiments. More importantly, we found that in most cases, only a small number of catalysts were used and reported studies on the subject showed that metal leaching could not be completely avoided. Thus, it still needs a lot of efforts to effectively promote the technology and put it into practice.

(6) Last but not least, it is necessary to combine experimental studies with computational simulations to further understand the relationship between structure and performance, and to provide theoretical basis for the rational design and development of new efficient catalysts. Therefore, the follow-up work can be carried out with the relevant experiments. Then, reasonable theoretical calculations, such as first-principles density functional theory (DFT) calculations, can be used to investigate the important structural features of new bimetallic catalysts, including electronic band structure, crystal surface energy and interface charge transfer process, etc.

Declaration of Competing Interest

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

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