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Copper-based non-precious metal heterogeneous catalysts for environmental remediation

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ABSTRACT

This paper presents a detailed review of copper-based catalysts used in wide-ranging environmental remediation, including gas, liquid and solid phase pollutant elimination. Latest advances in the remarkable catalytic activity of copper-based catalysts, including bulk CuO_x , supported CuO_x , and solid solution $\text{CuO}_x\text{-X}$ are emphasized. The structure-activity relationships among the crystal structure, morphology, catalyst support, and catalytic performance in specific catalytic reactions for environmental remediation are discussed. Furthermore, current obstacles faced by Cu-based catalysts and potential strategies to address them have been proposed, which may aid the future research and development of highly efficient Cu-based non-precious metal catalysts.

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1. Introduction

The rapid growth of the global economy and industrialization in the past century has caused serious environmental problems that greatly influence the sustainability of human society and seriously effect human health [1]. Gaseous, liquid, and solid pollutants are released from both industrial and mobile sources [2]. Carbon monoxide (CO) is toxic and detrimental to all respiring life forms, particularly humans [3], and contributes indirectly to atmospheric chemistry and subsequent global warming and ozone depletion. Nitrogen oxides (NO_x) [4] and sulfur dioxide (SO_2), generated by burning fossil fuels, vehicles, manufacturing, oil refineries, and other industries, are the main causes of acid rain, which has a severe effect on ecosystems and human health [5]. Volatile organic compounds (VOCs) are not only hazardous air pollutants, due to their toxic, malodorous,

mutagenic, and carcinogenic properties [6], but also precursors to ozone and smog due to their photochemical reactivity in atmosphere [7]. Industrial organic pollutants in wastewater, typically containing stable aromatic molecular structures that are difficult to degrade, are major hazards to the environment due to their toxicity and persistence [8]. As a solid pollutant, particulate matter is also harmful to human health because it can be inhaled deep into lungs and enter the bloodstream [9].

Tremendous effort has been made to control the release of pollutants due to growing concerns over climate change, our ecological footprint, and human health. Much of this research has concentrated on developing robust and highly efficient catalysts for environment remediation. Noble metal catalysts (Pt [3,4] and Pd [10]) are generally very active [11], but suffer from their high cost and severe activity degradation resulting from poisoning by contaminants, such as chloride compounds

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[12]. Transition metal oxides with impressive low-temperature catalytic activities are considered potential low-cost alternatives to precious metal catalysts [8,9]. Among them, copper and its oxides have attracted increasing attention as promising substitutes for precious metals in numerous industrial processes due to their high activities, low cost, and earth-abundant reserves [13,14].

Cu is a transition metal with a 3d electronic configuration that has some interesting physical and chemical properties. Cu-based materials can promote a variety of reactions, mainly due to their accessible oxidation states (Cu(0), Cu(I), and Cu(II)). Cu-based oxides are promising materials for broad applications, including catalytic organic transformations, electrocatalysis, and photocatalysis, mainly due to their high redox potential, environmental friendliness, and low cost. For environment remediation, Cu-based oxides have various applications as catalysts, including in the selective catalytic reduction (SCR) of NO_x using NH₃, catalytic combustion of VOCs, CO oxidation, organic pollutant degradation, and catalytic oxidation of soot [15]. The catalytic activity of Cu-based catalysts is highly dependent on its material composition, structure, and morphology. Based on the literature, Cu-based catalysts can be generally classified into three types: (i) bulk copper oxide (CuO_x), (ii) supported copper oxide (CuO_x/support), and (iii) solid solution copper oxide (CuO_x-X). As reduced use of precious metals is increasingly demanded, much research has focused on the rational fabrication of highly efficient copper oxide catalysts and elucidation of their active catalytic sites. However, reviews dedicated to summarizing recent progress in copper-based catalysts for heterogeneous catalytic reactions used in environmental remediation remain limited.

This review summarizes recent progress toward different Cu-based metal oxides for various typical environment remediation applications, including CO oxidation, selective NO_x reduction, VOC control, waste water treatment, and soot particulate removal. Herein, we provide insight into the intrinsic relationships between the crystal structure, morphology, catalyst support, and other features of copper oxides and their catalytic performance in specific catalytic reactions for environmental remediation. Furthermore, current obstacles facing towards the broad application of Cu-based catalysts, and potential strategies to address them, have been proposed to potentially shed light on the future research and development of highly efficient Cu-based non-precious metal catalysts.

2. Structures and properties of Cu-based catalysts

2.1. Bulk copper oxide (CuO_x)

Copper oxides (CuO_x) mainly exist as two stable oxides, namely, cupric oxide (CuO) and cuprous oxide (Cu₂O). These Cu-based oxides have various controllable crystal structures, morphologies, porosities, and textures, which contribute to a broad range of adjustable catalytic activities (Fig. 1). These structural parameters play a crucial role in their catalytic oxidation performance. Understanding the relationship between the structure characteristics and catalytic performance of

Fig. 1. Structures and morphologies of Cu₂O, CuO, supported CuO_x, and CuO_x-X catalysts.

Cu-based oxides is the first step in the rational design of high-activity catalysts.

Copper oxides with different valance states often have different catalytic performances in pollutant removal, with catalytic activity originating from one-electron (Cu²⁺↔Cu¹⁺, Cu¹⁺↔Cu⁰) or two-electron (Cu²⁺↔Cu⁰) pathways. Furthermore, different morphologies and crystalline structures of CuO and Cu₂O lead to different catalytic performances. For example, CuO mesoporous nanosheets have excellent CO oxidation catalytic activity shown to be 35 times that of commercial CuO powders at 200 °C (up to 47.77 mmol/(g·h)) [16]. The large specific surface area, mesoporous structure, low thickness (approx. 10 nm), and uniform exposed (002) crystal plane of these nanosheets are responsible for their increased active sites and simultaneous dramatic enhancement in activity [17,18]. The (002) plane of CuO nanosheets, terminated with an atomic Cu layer that gives rise to insufficient oxygen atoms coordinating with Cu atoms on the surface, is a close-packed plane with more dangling bonds that could potentially adsorb more CO gas. Furthermore, the lack of coordination between oxygen atoms and Cu atoms on the surface of the as-prepared CuO nanosheets also enhanced their catalytic activity [19]. Recent studies have developed novel synthetic methods, such as metal-organic chemical vapor deposition (MOCVD), laser ablation, hydrothermal processing, thermal oxidation, and the wet chemical method, to control the morphology and enhance catalytic performance [20].

Copper oxides in the form of cuprous oxide (Cu₂O) and cupric oxide (CuO) are p-type semiconductors with relatively low direct band gaps of ~2 and ~1.2 eV, respectively [21]. Much effort has been dedicated to adjusting the synthetic conditions for obtaining copper oxides (CuO_x) with desirable shapes, sizes, morphologies, and crystal structures to improve their catalytic performance [22]. Cu₂O has a face-centered cubic (*fcc*) crystal structure (space group, *O_h⁴-*pn*3*m*), in which oxygen atoms form*

a body-centered cubic lattice and copper atoms form a face-centered cubic lattice with a unit cell length of 4.27 Å, that is the active component of catalysts used for CO oxidation and VOC combustion. The optimized surface structures of low-index Cu₂O (100), Cu₂O (110), and Cu₂O (111) crystal planes have surface energies in the order (100) < (110) < (111) [11,12]. Numerous Cu₂O nano- and microstructures with well-controlled uniform morphologies have recently been synthesized, including (111) octahedra [23], (100) cubes [24], (100) truncated octahedra [25], rhombic dodecahedra [26], (110) truncated octahedra, (100) truncated rhombic dodecahedra, nanowires, nanoplates, nanocages, and branched and hollow structures. On Cu₂O (100), the topmost layer consists of two-coordinated O and Cu atoms on the surface that are coordinatively saturated. On Cu₂O (110), the topmost layer consists of three-coordinated O and Cu atoms, while the second layer consists of Cu. The Cu₂O (100) surface is more stable than the Cu₂O (111) surface due to the terminated coordinated Cu atoms with abundant d-electrons on the Cu₂O (111) surface. On Cu₂O (111), the topmost layer consists of three-coordinated O and the second layer consists of Cu (75%) and singly-coordinated unsaturated Cu (25%). Cu atoms on the (111) surface are usually coordinatively unsaturated with more dangling bonds for the adsorption of ionized oxygen species, which are responsible for the high activity [27]. CuO is a semiconducting oxide that crystallizes in the complex monoclinic tenorite structure with Cu-O planes. Several different CuO morphologies, such as nanowires [28], nanotubes [29], ribbons [30], flower shapes [31], nanorings [28], and hollow microspheres [32], can be fabricated under different synthetic conditions. The close-packed low-index (111) planes of the oxides have lower free energies and higher stabilities than the more open (001) and (011) planes. The reactivity on the crystal surfaces is correlated with the surface energy, which had an observable effect on the oxygen chemisorption energy at CuO surfaces. Furthermore, high-index planes of CuO_x nanomaterials are terminated by an atomic Cu layer, which gives rise to coordinatively unsaturated Cu atoms on the surface. In addition, the close-packed plane with more dangling bonds could potentially adsorb more CO gas [19].

2.2. Supported copper oxide (CuO_x/support)

Supported copper oxide (CuO_x/support), typically comprising CuO_x primary active sites and a high surface area support, such as CeO₂ and zeolite, is a common composite catalyst with enhanced performance in various heterogeneous catalytic reactions. Generally, these supports have multiple roles. First, the support enlarges the surface area available for CuO_x active sites. The catalyst support provides a very large surface area over which active sites are dispersed efficiently, which can prevent particle aggregation and the associated degradation in catalytic activity. Furthermore, the catalyst support can provide space for the catalytic reaction to occur. For example, activated carbon is often used as a catalyst support to provide space for active sites and the catalytic reaction [33]. Second, the supports can improve the catalytic properties of the composite catalyst

by participating in the reaction via promoting charge transfer or the O₂ storage capacity [34]. CeO₂ can enhance O₂ storage performance, which is beneficial for gaseous pollutant adsorption and catalytic oxidation. Third, due to a synergy effect, the interface between the catalyst and support may contain new active sites for the efficient absorption of molecular reactants or favor fast charge transfer, with the reversible oxidation capability then further enhancing the intrinsic catalytic activity of the composite catalysts. For instance, the quick reversible redox process of superficial Cu(I)/(II) couples in a strong synergistic interaction with a nanocrystalline ceria support at the interface between the active Cu sites and ceria is responsible for its low-temperature catalytic activity.

According to the literature, supports that have been used with CuO_x include Al₂O₃, CeO₂, and Ce-Zr solid solutions. These catalytic supports can be classified into two categories: inert supports and functional supports. Inert supports, such as Al₂O₃ [35] and zeolites [36], do not take part in the catalytic reaction and only supply space for the catalytic reaction or improve the dispersion of CuO_x particles. In contrast, functional catalyst supports, such as CeO₂ [37] and Ce-Zr solid solutions [38], often act as adsorption sites for the reaction. The unique ability of Ce⁴⁺/Ce³⁺ and ensuing oxygen vacancy generation are key factors in its application to heterogeneous catalysis. Compared with CeO₂, Ce-Zr solid solutions can better enhance O₂ storage performance, which makes Ce-Zr solid solution the most used non-carbon catalytic support in various catalytic reactions. Although many different catalyst supports have been reported, their basic function remains promoting the high dispersion of active Cu sites on composite catalysts.

2.3. Solid solution copper oxides (CuO_x-X)

Solid solution metal oxide (CuO_x-X) catalysts are of great interest due to their modifying effects on copper oxides, which can enhance the thermodynamic stability, electronic properties, and surface properties. These modifying elements are mainly transition metal elements and rare earth elements. Most transition metal oxides, such as TiO₂, MnO_x, and CoO_x, also show catalytic performance for pollutants. Composites of CuO_x and these transition metal oxides could synergistically enhance the catalytic performance of the system. In general, CuO often suffers from SO₂ poisoning and low reactivity at high temperatures. With the addition of transition metal oxides, Ti-CuO_x can protect CuO from SO₂ poisoning [39]. In many cases, CuO has a higher catalytic performance at low temperature. Moreover, with the addition of FeO_x [40,41] or CoO_x [42], the high-temperature activity can be enhanced. Some main group elements, such as Zr [43] and Sn [44], have commonly been used to modify CuO. Both these oxides have nearly no activity in catalytic reactions. However, the incorporation of main group elements into CuO_x enhances the properties of CuO. CeO₂ has excellent oxygen storage performance and can capture gaseous O₂ from flue gas to form adsorbed oxygen, which means it could offer suitable adsorption sites for gaseous pollutants. Recently, ternary composite oxides and multicomposite oxides have been developed to further enhance the performance of CuO. A ter-

nary mixed oxide catalyst composed of copper oxide, cobalt oxide, and ceria showed superior catalytic performance in CO oxidation [45]. The ability to separate the active sites of CO and hydrocarbons (CH_x) might drastically reduce the inhibition effects. Understanding the role of each element and the interaction of these elements is beneficial for the rational design of highly efficient Cu-based catalysts. Furthermore, element doping in copper oxides could change the local charge conditions and enhance sulfur resistance [46], propene resistant [45], and the low-temperature catalytic activity [47].

3. Copper-based catalysts for gas phase pollutant control

3.1. Recent advances in copper-based catalysts for CO oxidation

Carbon monoxide is usually generated by the incomplete combustion of fossil fuels [48]. Copper oxides, such as Cu_2O and CuO , are known to exhibit high activities in the oxidation of CO. Huang et al. [49] investigated the catalytic combustion performance of CO over copper oxide catalysts (Cu_2O and CuO). The results indicated that their catalytic activities were in the order $\text{Cu}_2\text{O} > \text{metastable cluster CuO} > \text{CuO}$, which correlated with valence variations and the ability to seize or release the surface lattice [50]. Compared with fresh Cu_2O catalysts, the higher surface concentration of active chemisorbed oxygen and corresponding improved interaction with CO contributed to the

dramatically enhanced activity on the samples used [51]. The shape and exposed crystal planes have been shown to play an important role in the catalytic oxidation of CO. Surface oxygen vacancies, generated by coordinately unsaturated Cu atoms on the surface, can adsorb ionized oxygen species and react with the reducing gas more readily. Truncated concave octahedral Cu_2O enclosed mainly by (332) high-index facets exhibited enhanced catalytic activity compared with low index (111) and (100) facets, which could be due to the presence of high-density steps on the (332) high-index facets. The CO catalytic activities of the crystal facets were found to be in the order (332) > (111) > (100) [22]. Similar facet-dependent CO oxidation catalytic activity has also been observed on CuO . CuO nanoplatelets with exposed (011) planes more easily release oxygen from the surface lattice, followed by nanobelts with (001) planes, which, in turn, are more active than nanoparticles with close-packed (111) planes [52]. As morphologies play an important role in determining the properties of nanostructured materials, Huang et al. [19] devoted much effort to engineer the morphologies of CuO nanostructures and synthesize nanosheets with high-index (002) facets exposed, as shown in Fig. 2(a) and (b). The catalytic activity of these CuO mesoporous nanosheets in CO oxidation was found to be up to 47.77 mmol/(g·h), which is about 35 times higher than that of commercial CuO powders at 200 °C, (Fig. 2(c)). As shown in Fig. 2(d), the low apparent activation energy (53.3 kJ/mol) of the

Fig. 2. (a) Scanning electron microscopy (SEM) and (b) high-resolution transmission electron microscopy (HRTEM) images of a CuO nanosheet; (c) CO oxidation conversion light-off curves using CuO nanosheets; (d) Arrhenius plots for the reaction activation energy (E_a) on CuO nanosheets and Zn_4Cu_2 nanoparticles. Adapted from Ref. [19].

CuO nanosheets further evidenced the high catalytic activity for CO oxidation. The exposed crystal plane was assigned to the (002) crystal plane of the CuO nanosheet, which was vital to its superior catalytic performance because of the terminated coordinatively unsaturated atomic Cu layer on the surface. The close-packed plane with more dangling bonds could possibly adsorb more CO gas. Furthermore, the lack of oxygen atoms coordinated to Cu atoms on the surface of this CuO nanosheet could also enhance its catalytic activity [19].

Copper-manganese oxides supported on multiwalled carbon nanotubes (MWCNTs) have been synthesized as efficient catalysts for low-temperature CO oxidation [53]. The temperature for total CO conversion (T_{100}) on these catalysts was 200 °C and the half-conversion temperature (T_{50}) was stable at 63–70 °C, which was much lower for CuO-MnO₂ bimetallic catalysts with half CO conversions of 83.9–196.4 °C. The synergistic interaction within the bimetallic Cu-Mn catalytic system, high surface area, and large pore volume are responsible for its enhanced activity for CO oxidation.

Since the groundbreaking work of Flytzani-Stephanopoulos et al. [54], regarding the catalytic oxidation of CO using even physical mixtures of CuO and CeO₂ as catalyst, low-temperature CO oxidation mediated by CuO/CeO₂ catalysts has been extensively investigated. CeO₂ in contact with Cu²⁺ facilitates the formation of Cu⁺ due to the Ce⁴⁺/Ce³⁺ redox process, which can transfer electrons to Cu²⁺ to form Cu⁺. This enhances CO adsorption, leading to the excellent catalytic activity [55–59]. Solid-solution Cu_yCe_{1-y}O_{2-x} and mixed-phase CuO/Cu_yCe_{1-y}O_{2-x} catalysts are particularly promising for CO oxidation under ambient conditions, Cu_{0.1}Ce_{0.9}O_{2-x} exhibited the highest activity among catalysts measured, with a computed oxygen vacancy formation energy (E_{vac}) of 0.85 eV [59]. In contrast, CuO/Cu_{0.05}Ce_{0.95}O_{2-x} catalyst showed a CO oxidation rate of 0.2 μmol/(s·g) at 45 °C, making it the most active CuO_x/CeO₂ composite catalyst among those reported [60]. To further understand the generally recognized synergistic effects in CuO-CeO₂ catalysts, Luo et al. [61] concluded that finely dispersed species possessed the highest activity, bulk CuO species had medium activity, while Cu²⁺ in the CeO₂ lattice had the lowest activity. Cu-Ce mixed oxides prepared by microemulsion-coprecipitation showed better catalytic performance than that prepared by an impregnation method due to structure related activity in nanostructured copper-ceria-based CO oxidation catalysts.

When doped with Cu²⁺, markedly improved catalysis is observed owing to homogeneous incorporation of Cu²⁺ into the CeO₂ lattice. The T_{50} values for CO using Cu_{0.1}Ce_{0.9}O_{2-δ} and Cu_{0.04}Ce_{0.96}O_{2-δ} were 83 and 95 °C, respectively [62–64]. The superior catalytic activity of the CuO_x/CeO₂ catalyst system in CO oxidation at low temperatures can be attributed to the quick reversible redox process of superficial Cu(I)/(II) couples in a strong synergistic interaction with the nanocrystalline ceria support [65]. Copper ions migrate out of the CeO₂ crystallite and aggregate on the CeO₂ surface, which results in a lower coordination environment that enhances the reducibility of Ce⁴⁺/Ce³⁺. In Scheme 1(a), steps I and II illustrate the reaction mechanism of CO oxidation over bulk CuO, in which CO₂ is generated from the oxidation of CO by Cu(II), resulting in the formation of a Cu(I) species, which is oxidized by O₂ to complete the catalytic cycle. Steps III and IV describe the role Ce⁴⁺/Ce³⁺ ion pairs play in the reaction. The reduced Cu species (CuI) are reoxidized at the Cu/CeO₂ interface by CeO₂-mediated oxygen transport and form oxygen vacancies that can be filled by adsorbed O₂ to complete the recycle. This redox cycle promotes the ability of copper ions to adopt different oxidation states and supply oxygen [37]. The redox relationship between copper and cerium in the catalyst is key to understanding the reaction mechanism and improving the catalytic performance [58]. Scheme 1(b) shows the CO oxidation mechanism on Cu₂O, which suggests that Cu₂O is more active for CO oxidation than Cu (111) due to the higher CO adsorption energy on Cu₂O. This inhibits oxygen poisoning because of the significant difference between CO and O adsorption energies [66].

Although Cu₂O has superior CO oxidation activity at low temperatures, poor thermal and hydrothermal stability are the main obstacles to its broad industrial application. To understand how to stabilize the CuO_x, Baber et al. [67] fabricated TiCuO_x films by depositing titanium onto a Cu₂O(111) film at 300 K. The as-prepared TiCuO_x film exhibited excellent low-temperature activity and stability in CO oxidation, as shown in Fig. 3(b). An atomically resolved scanning tunneling microscopy (STM) image of a hexagonal island (Fig. 3(a)) exhibited a Moire structure (1.82 ± 0.15 nm) and a close-packed hexagonal structure (0.28 ± 0.02 nm). Density functional theory (DFT) calculations are presented in Fig. 3(b) and (d), in which most of the copper atoms located on the surface have separated by long distances of 0.894 nm. The long distance between each surface

Scheme 1. Proposed mechanism for CO oxidation over (a) CuO/CeO₂ (adapted from Ref. [58]) and (b) Cu₂O (adapted from Ref. [66]).

Fig. 3. (a) Scanning tunneling microscopy (STM) images and low-energy electron diffraction (LEED) pattern of a TiCuO_x film; (b–d) Comparison of structures predicted by density functional theory (DFT) calculations with an STM image of TiCuO_x terraces; (e) Arrhenius plot of CO oxidation on Cu₂O and TiCuO_x films. Adapted from Ref. [67].

Cu⁺ cations in the mixed oxide inhibits facile dissociation of the adsorbed oxygen molecules, which prevents further oxidation of Cu⁺ active sites to Cu²⁺. DFT calculations was used to determine the complex catalytic behavior of CuTiO_x mixed oxides during CO oxidation [68]. The Cu⁺ ions were separated by the structural frame of TiO_x and the strong interaction (electronic effect) at –Cu–O–Ti– interfacial sites led to the reduction of Ti⁴⁺, which enhanced activity toward O₂. The unique structural frame of CuTiO_x was able to stabilize and isolate a single Cu⁺ site on the terrace, which was proposed to be active for CO oxidation.

Copper oxide-based catalysts, such as hopcalite (CuMn₂O₄), are among the most active catalysts for low-temperature CO oxidation. Recently, Tang et al. [69] synthesized nanocrystalline copper manganese oxide catalysts using the supercritical anti-solvent precipitation method that showed catalytic activity more than two times higher than conventionally prepared hopcalite catalysts for CO oxidation [70]. They attributed this high catalytic activity to the nanocrystalline and homogeneous nature of the synthesized copper manganese oxides.

A ternary mixed oxide catalyst composed of copper oxide, cobalt oxide, and ceria (denoted CCC) outperforms synthesized and commercial platinum group metal (PGM) catalysts for CO oxidation in simulated exhaust streams, while showing no sign of inhibition by propene [45]. The enrichment of Cu⁺ on the surface of CuO–Co₃O₄–CeO₂, resulting in a stronger interaction between Co₃O₄ and CeO₂ and the appearance of oxygen vacan-

cies in CeO₂, afforded higher catalytic activity in CO oxidation compared with catalysts heated at different temperatures [71]. Cu⁺ ions are proposed to be active sites and form Cu⁺–CO species, while lattice oxygen located at the Co₃O₄–CeO₂ interface is proposed to be the origin of active oxygen [72].

3.2. Selective catalytic reduction (SCR) of NO_x using NH₃

The abatement of environmentally harmful NO_x compounds (NO, NO₂, and N₂O) emitted from mobile and stationary power sources remains a challenging task in the field of catalysis. The removal of nitrogen oxides (NO_x) has received more attention in past decades because NO_x are known to cause many environmental problems, including acid rain and photochemical smog in urban and industrial areas [17,73]. The selective catalytic reduction (SCR) of NO_x using ammonia has been the subject of extensive research [74]. The basic SCR reaction can be described as follows 4NH₃ + 4NO + O₂ → 4N₂ + 6H₂O.

V₂O₅–WO₃/TiO₂ is the traditional catalyst for the commercial SCR of NO_x using ammonia (NH₃–SCR). However, its drawbacks, including a narrow working temperature range, the use of toxic vanadium species, and low N₂ selectivity at high temperatures [75], have motivated a new wave of innovation toward more efficient and environmentally friendly alternative catalysts for NH₃–SCR–NO_x. Among various attempts, copper-based catalysts supported on oxides or zeolites have recently emerged as attractive candidates due to their environmentally benign char-

acteristics and high SCR performance in a wide temperature range with good selectivity [76,77].

Supported copper oxides fabricated by dispersing active Cu species on large surface area supports have been widely studied in NH_3 -SCR catalysis. Molecular sieves (such as zeolites, ZSM-5, SBA-15, and SSZ-13), Ce-Zr solid solutions, and metal oxides (such as V-based oxides, TiO_2 , and Ce- TiO_2) are widely used as supports. Molecular sieves have complex structures with microporous-mesoporous characteristics and specific surface properties responsible for enhancing catalytic performance and thermal stability [77,78]. Cu-promoted zeolites, such as Cu-ZSM-5, Cu-BEA, and Cu-FER, have shown superior low-temperature (<300 °C) conversion and selectivity in NH_3 -SCR and direct NO decomposition. Iwamoto et al. [80] synthesized a series of metal (Zn, Mg, Co, and Cu) oxides on a ZSM-5 support, among which Cu^{2+} -exchanged zeolites appeared to be more active for NO decomposition. The high dispersion of CuO and high surface acidity of the catalyst were found to be responsible for the high de- NO_x performance. Compared with Cu-ZSM-5 catalysts, a Cu^{2+} ion-exchanged beta zeolite (Cu-beta) has been shown to have higher activity in the SCR of NO_x using NH_3 , with metal-exchanged beta zeolites generally found to have improved hydrothermal stability. The en-

hanced catalytic performance is due to the higher copper valence and lattice oxygen mobility compared with the Cu/ZSM-5 catalyst [81]. Having met the activity and durability requirements of the automotive industry, Cu^{2+} -exchanged molecular sieves with chabazite (CHA) structures, such as Cu-SSZ-13 and Cu-SAPO-34, have been commercialized as NO_x after-treatment catalysts in diesel-powered engines for transportation. SSZ-13 is appropriate for use in the SCR of NO using NH_3 due to its adjustable pore diameter, thick pore walls, and excellent hydrothermal stability [60,82]. As shown in Fig. 4(a), the NO_x conversions of these catalysts in the high-temperature region (350–550 °C) were in the order Cu-SSZ-13 > Cu-ZSM-5 > Cu-beta. At reaction temperatures above 300 °C, Cu-ZSM-5 and Cu-beta produced significant amounts of NO_2 and N_2O , while at 500 °C the amounts of NO_2 and N_2O produced over these two catalysts were 30 and 25 ppm, respectively, which was much higher than the <10 ppm measured over Cu-SSZ-13 (Fig. 4(b) and (c)). As shown in Fig. 4(d), Cu-SSZ-13 has the best resistance toward SO_2 and C_3H_6 poisoning. The pore size of SSZ-13 (3.8 Å) was smaller than the kinetic diameter of C_3H_6 (4.678 Å), which provided a size restriction for gaseous molecules. Therefore, active sites located inside the channel can still operate without being affected by C_3H_6 introduction [83,85].

Fig. 4. (a) NO_x conversion profiles for Cu-SSZ-13 (1), Cu-beta (2), and Cu-ZSM-5 (3) at various temperatures; (b) NO_2 and (c) N_2O formation profiles during NH_3 -SCR on Cu-SSZ-13 (1), Cu-beta (2), and Cu-ZSM-5 (3), adapted from Ref. [78]; (d) NO_x conversion of Cu-zeolites (Cu-SSZ-13 (1), Cu-ZSM-5 (2), Cu-beta (3)) with C_3H_6 and SO_2 , adapted from Ref. [79].

SSZ-13 exhibits the highest SO_2 to SO_3 conversion, hindering the generation of more stable CuSO_4 , which could cause serious deactivation. At least three NH_3 adsorption sites, including two distinct populations of exchanged Cu sites and Brönsted acid sites, have been identified in Cu-SSZ-13, and are responsible for the enhanced catalytic performance [84]. The differences in activity and selectivity of the three zeolites above may be related to the fundamental structural characteristic of these zeolites, namely, the pore sizes and locations of the copper ions. The order of high-temperature NH_3 -SCR reactivity discussed earlier was the inverse of the zeolite pore size order. SSZ-13 produced the most active catalysts with the smallest pores (~ 4 Å, 8-membered ring) and ZSM-5 showed medium activity with medium-size pore openings (~ 5.5 Å, 10-membered ring). Meanwhile, beta zeolite had the lowest activity and N_2 selectivity with the largest pores (~ 7 Å and ~ 5.5 Å, 12-membered ring). For these catalysts, the smaller pore sizes seemed to favor the desirable reaction pathways. However, detailed mechanistic studies and experimental results are needed to verify the correlation between pore size and activity/selectivity. In summary, both the activity and selectivity of Cu-SSZ-13 for NO_x -SCR using NH_3 are superior to those of Cu-ZSM-5 and Cu-beta over the entire temperature range studied (up to 550°C). The catalytic activity can be further improved by preparing composite catalysts. The addition of cerium [76] and zirconia [87] increased the copper dispersion and prevented its crystallization, which improved the redox properties of the CuCe/ZSM-5 catalysts. As shown in Fig. 5(a), the light-off temperature (10% NO conversion) was about 103°C for Cu/ZSM-5 (Cu-Z), while the value shifted to 60°C when the cerium content was increased in 2%Cu+2%Ce sample (CuCe4-Z). An NO conversion of 95% was reached at around 197°C for Cu-Z, while the corresponding temperature was decreased to 148°C for CuCe4-Z. According to Fig. 5(b), Cu-Zr exhibited excellent activity in SCR, with NO conversions above 95% in the temperature range 197 – 404°C . When appropriate amounts of zirconium were added to Cu/ZSM-5, the temperature range for efficient NO reduction ($>95\%$) was extended to both lower and higher temperatures.

Cu-SSZ-13 powder catalysts with various ion-exchange lev-

els were characterized to illustrate the relationship between catalytic performance and structure. As shown in Fig. 6(a), at low ion-exchange (IE) levels (such as $\text{IE} = 23\%$), there was only one Cu^{2+} ion within each hexagonal unit cell. In this case, hydrated Cu^{2+} ions were octahedrally coordinated at subambient temperatures, suggesting they were still coordinated to lattice oxygen atoms of the 6-membered rings [88]. As the Cu loading increased, it was possible that two Cu^{2+} ions could sit in one unit cell [89]. Some Cu^{2+} ions were located in the large CHA cages and close to 8-membered rings (Fig. 6(b)). Standard NH_3 -SCR reaction kinetics were measured at high-space velocities, which demonstrated that the reaction kinetics were controlled by intraparticle diffusion limitations [90]. These results suggested that, for the CHA SCR system, both washcoat and pore diffusion limitations should be considered for optimum practical application. The reaction rates increased with increasing Cu loadings due to weaker interactions between the Cu ions and zeolite framework at higher Cu loadings, which allowed more facile $\text{Cu}^{2+} \leftrightarrow \text{Cu}^+$ redox cycling. Recent research showed that NH_3 -solvated Cu^{I} ions have sufficient mobility to travel through 8-membered ring zeolite windows and form transient ion pairs that participate in an O_2 -mediated $\text{Cu}^{\text{I}} \rightarrow \text{Cu}^{\text{II}}$ redox [91]. As shown in Fig. 6(c), N_2 , H_2O , and $\text{Cu}^{\text{I}}(\text{NH}_3)_2$ were produced by the reduction of NO and NH_3 by NH_3 -solvated Cu^{II} ions charge-compensating for either one (left cycle) or two (right cycle) framework Al sites. Mobile $\text{Cu}^{\text{I}}(\text{NH}_3)_2$ species can diffuse and be oxidized by O_2 to generate the Cu^{II} dimer intermediate.

In addition to zeolite, many metal oxides are commonly used as catalyst supports for copper oxide [92]. Al_2O_3 -based supports are the most studied materials in the NH_3 -SCR reaction [9]. Pure Al_2O_3 has no activity in the NH_3 -SCR reaction, mainly providing a high surface area to aid CuO_x dispersion on its surface and enhance catalytic performance.

$\text{CuO}_x\text{-X}$ represents a series of solid-solution composite copper oxides that have high activity for NO, where X can be CeO_2 and Cu-Mn mixed oxides. Ce is the most used element for the modification of CuO_x . CeO_2 is well known to have labile oxygen vacancies and bulk oxygen species with relatively high mobili-

Fig. 5. (a) Catalytic activities for NO reduction using NH_3 of pure ZSM-5, Cu-Z, CuCe1-Z, CuCe2-Z, CuCe3-Z, and CuCe4-Z catalysts, adapted from Ref. [76]; (b) SCR activity from NO_x conversions as a function of reaction temperature for V-W/ TiO_2 , Cu-Z, and CuZr-Z catalysts, adapted from Ref. [87].

Fig. 6. (a) Schematic of the SSZ-13 hexagonal unit cell structure and possible Cu²⁺ locations, adapted from Ref. [73]; (b) Corresponding structure of Cu-SSZ-13 obtained from refinement and magnification of the d6r unit with Cu present as an isolated ion, adapted from Ref. [89]; (c) Proposed low-temperature SCR catalytic cycle, adapted from Ref. [91].

ty, and is easily formed during the redox shift between Ce⁴⁺ and Ce³⁺ under oxidizing and reducing conditions, respectively. Incorporation with CuO_x could enhance the performance of CeO₂, for which the mechanism has been widely studied. The modulated distribution of Cu⁺ achieved by adjusting the Ce/Cu molar ratio was found to be crucial for optimizing the redox ability and acid properties. Outstanding SO₂-resistant NH₃-SCR performance (NO conversion close to 100% in the temperature range 250–350 °C under 200 ppm SO₂) has been observed using (CeO_x)_{0.25}CuO as catalyst [93].

3.3. Catalytic activity of copper-based catalysts for VOC oxidation

Volatile organic compounds (VOCs), emitted by various industrial processes and transportation activities, are considered important contributors to secondary particulate matter and atmospheric oxidants. Catalytic oxidation is among the most developed techniques for VOC elimination, as it requires lower energy consumption and emits less NO_x than thermal oxidation [94]. Metal oxides of Cu [95], Cr [96], and Co [97] are low cost alternatives to noble metals as catalysts for VOC oxidation with competitive performance.

Copper oxides are known to exhibit high catalytic activity in the oxidation of hydrocarbons. The morphology and shape of Cu₂O had been shown to greatly influence the CH_x oxidation activity. Huang et al. [98] investigated the crystal-plane-controlled catalytic performance uniform capping-ligand-free Cu₂O octahedra, cubes, and rhombic dodecahedra in propylene oxidation with O₂. As shown in Fig. 7, the results indicated that

Cu₂O cubes with exposed (100) crystal planes were the most selective for CO₂.

Mixed metal oxides have been widely applied in the catalytic combustion of VOCs. Copper and yttrium-doped zirconia have been prepared and tested for the combustion of propene and toluene [99]. The results indicated that total combustion of propene and toluene was achieved at 350 °C. This support should favor the formation of CuO particles that should be the active catalytic sites. 0.5%Pd-NaFAU zeolite and 5%Cu-ZrO₂ were found to be promising catalysts for complete toluene oxidation. The activity of copper oxide was somewhat correlated to the oxygen mobility of the support, leading to easily reducible small copper species.

CuO-CeO₂ has been shown to be a powerful catalyst for oxidation reactions that is even comparable to supported noble metal catalysts due to the introduction of ceria, which stabilizes the active Cu sites, affecting Cu redox [61]. Plenty of Cu²⁺ ions in mesoporous CuCeO_x oxides were shown to be incorporated into the CeO₂ lattice in the form of a Cu_xCe_{1-x}O_{2-σ} solid solution, which produced large amounts of oxygen vacancies at CuO_x and CeO₂ interfaces. Meanwhile, the Cu²⁺-O²⁻-Ce⁴⁺ connection in the solid solution can act as a bridge for oxygen transfer between Cu and Ce, and enhance the reducibility of both components [100]. Hu et al. [101] have reported the high activity of a CuO-CeO₂ (10 at% Cu) catalyst in benzene oxidation. A higher calcination temperature would lead to more Cu²⁺ species and richer lattice oxygen species on the surface of the catalysts, which are favorable for benzene oxidation.

Al₂O₃-supported CuO_x has been prepared and tested in the combustion of VOCs, including methanol, ethanol, acetalde-

Fig. 7. Conversion and selectivity for propylene oxide, acrolein, and CO₂ in C₃H₆ oxidation with O₂ as catalyzed capping-ligand-free catalysts. (a) Cu₂O cubes, (b) octahedra, and (c) rhombic dodecahedra. (d) Specific reaction rate of C₃H₆ oxidation with molecular oxygen catalyzed by capping-ligand-free Cu₂O cubes (c-Cu₂O), octahedra (o-Cu₂O), and rhombic dodecahedra (d-Cu₂O). Adapted from Ref. [98].

hyde, formic acid, and acetic acid [102]. The VOCs were typically adsorbed on the alumina surface, diffused, and then reacted on the CuO surface. Lattice oxygen in CuO is active for deep oxidation and, as lattice oxygen is depleted, the diffusion of lattice oxygen to the surface limits the oxidation rate. Supported CuO oxidizes VOCs with the order of reactivity as follows: HCOOH > CH₃OH > CH₃COOH > C₂H₅OH > C₂H₄O. Águila et al. [35] prepared a series of ZrO₂, Al₂O₃, and SiO₂-supported copper oxide catalysts for the complete oxidation of methane. Among these, the better catalytic performance of ZrO₂-supported copper oxide was related to the capacity of zirconia to stabilize highly dispersed Cu species. Activated carbon (AC)-supported CuO catalysts were prepared using an incipient-wetness impregnation method, resulting in a benzene removal efficiency of more than 80% when the inlet concentration ranged from 78 to 409 ppm. The high surface area (483.8 m²/g) and well-developed porosity (0.37 mL/g) of these catalysts governed their catalytic activity in benzene oxidation [33].

CuO-CeO₂ materials are effective oxidation catalysts due to the promoting effect of ceria, which possesses a high oxygen

storage capacity and a facile Ce⁴⁺/Ce³⁺ redox cycle. Larsson et al. [94] have studied the oxidation of ethanol and ethyl acetate over CuO/TiO₂ and CuO-CeO₂/TiO₂ catalysts. The interaction between cerium and copper results in improved reducibility of the active copper oxide species, which explains the improved catalytic activity. The facile Ce⁴⁺/Ce³⁺ cycle promoted copper reduction to generate predominantly Cu²⁺ species. Several CuO-CeO₂ catalysts have been prepared via the combustion method and their catalytic performance examined in the oxidation of ethanol, ethyl acetate, and toluene [104]. Cu-MnO_x mixed oxides were also synthesized for the catalytic combustion of propane and ethanol [105]. The mixed oxides were prepared through coprecipitation at aging time of 4, 18 and 24 h. The catalytic activities of the Cu-Mn mixed oxides in the total oxidation of propane indicated that the catalytic performance of Cu-MnO_x binary metal oxides was better than that of pure Mn₂O₃ and CuO oxides. Furthermore, an increase in aging time could enhance the activity and selectivity for CO₂ [106]. A Cu-Mn-Ce ternary mixed oxide catalyst has been prepared using a citric acid sol-gel method [103]. As shown in Fig. 8(a), this

catalyst had a Cu-Mn-Ce molar ratio = 1:2:4 and produced the highest catalytic activity, with 99% toluene conversion achieved at temperatures below 220 °C. Fig. 8(b) shows that the coexistence of Cu-Mn mixed oxides and the ceria-based solid solution resulted in a strong synergetic interaction that promoted catalyst reducibility, increased oxygen mobility, and enhanced the formation of abundant active oxygen species. Surface and lattice oxygen in the CeO₂-based solid solution were transported as active oxygen. Furthermore, organic molecules (benzene) were adsorbed and activated by highly dispersed surface Cu-Mn mixed oxides, which acted as catalyst oxidation centers. The resulting structure was highly active for the catalytic combustion of VOCs [107,108].

4. Copper-based catalysts for the degradation of organic pollutants in wastewater

Wastewater from industrial processes contains organic pollutants that can not only damage the aquatic environment, but also impact the entire ecosystem. These organic pollutants can be classified as organic pesticides, polycyclic aromatic hydrocarbon petroleum pollutants, and organic matter. Most of these compounds are carcinogenic and have been listed as toxic priority pollutants by the European Union and USA. Among various water remediation technologies, advanced oxidation processes (AOPs), which are based on the generation of reactive oxygen species (ROS), are regarded as effective technologies for the degradation of hazardous organic pollutants in wastewater. Compared with homogeneous catalysts, highly efficient heterogeneous catalysts have received more attention due to their easy separation and recycling from the liquid reaction system. The degradation of persistent organic pollutants using heterogeneous Fenton-like processes has received significant attention. The Fenton process is an AOP that uses ferrous ions and hydrogen peroxide to generate the second most powerful oxidant, hydroxyl radicals, in aqueous solution. Copper has multiple redox states and the ability to decompose H₂O₂ into HO· via conventional Fenton-like pathways [109]. Therefore, a catalyst containing copper can undergo a heterogeneous Fenton-like process in the presence of hydrogen peroxide and

organic pollutants.

Angi et al. [110] synthesized copper oxide nanoparticles by sonicating copper acetate monohydrate with hydrogen peroxide. The heterogeneous Fenton activity of the prepared material for the degradation of methylene blue was also tested. The rate of dye removal was very high, perhaps due to the synergistic effect between CuO and H₂O₂ molecules, which facilitates fast decomposition of H₂O₂ to HO· radicals [111].

Copper loaded on various supports has also shown high Fenton-like catalytic activity. Supported copper oxides were synthesized to enhance the dispersion of Cu active sites. Zhang et al. [112] fabricated a porous CuO-γ-Al₂O₃ heterogeneous catalyst that offered superior activation efficiencies and good operational stability. Porous γ-Al₂O₃ played an important role in the dispersion of CuO particles, minimization of copper ions leaching into the liquid phase, and generation of Cu-OH complexes on the surface, which is the critical step for heterogeneous activation of H₂O₂ via the certain amount of basic surface sites on γ-Al₂O₃. Zeolite is a promising catalyst support with microporous-mesoporous characteristics and specific surface properties. Ghosh et al. [113] loaded Cu nanoparticles onto SBA-15 for the removal of various dyes, such as 4-nitrophenol, methyl orange, congo red, rhodamine B, methylene blue, and mixtures of dyes, in the presence of excess NaBH₄. This material exhibited high catalytic activity in the degradation of both single and mixed dyes, with dyes were removed within 8 min with high first-order reaction rate constants. Pradhan et al. [114] synthesized a mesoporous Cu/Al₂O₃-MCM-41 nanocomposite and applied it as a heterogeneous photo Fenton-like catalyst for the degradation of phenol, 2-chloro-4-nitrophenol and 4-chloro-2-nitrophenol in aqueous solution. Under low pH conditions (pH = 4), nearly 100% degradation of all phenolic compounds was achieved within 45 min. This catalyst was very efficient in the presence of sunlight, mainly due to its small particle size, easy copper reducibility, Cu²⁺ stabilization on the mesoporous Al₂O₃-MCM-41 support, good textural properties, and higher activity under visible light. Ordered mesoporous carbon is another interesting support due to its large specific surface area, uniform pore size, and accessible mesopores [115]. A catalyst of iron-copper bimetallic nanoparticles em-

Fig. 8. (a) Light-off curves and (b) mechanism of toluene combustion over Cu-Mn-Ce mixed-oxide catalysts, adapted from Ref. [103].

bedded within an ordered mesoporous carbon composite (CuFe-MC) was synthesized via a self-assembly strategy as an effective and stable heterogeneous Fenton catalyst for the degradation of organic contaminants [116]. The high dispersion of iron-copper bimetallic nanoparticles in the ordered mesoporous carbon increased the amount of active sites. Furthermore, ordered mesoporous carbon used as a supporting material can also activate H_2O_2 to generate $\cdot\text{OH}$ species, which are the active sites in the Fenton process.

Copper ferrite (CuFe_2O_4), a magnetic spinel material with cubic structure, is a promising catalyst due to its medium saturation magnetization, excellent chemical stability, and mechanical strengths. The porous structure and high specific surface area of the catalyst afforded superior catalytic performance for the removal of imidacloprid [119]. Wang et al. [118] synthesized highly ordered mesoporous copper ferrite (meso- CuFe_2O_4), which possessed a high specific area ($122 \text{ m}^2 \text{ g}^{-1}$) and well-ordered mesoporous structure, as shown in Fig. 9(b) and (c), which contributed an enhanced number of active sites and benefitted the adsorption and mass transfer of large molecules. As shown in Fig. 9(e) and (f), the catalytic activity of catalysts with ordered mesoporous structures was superior to those of nonmesoporous structures (meso- $\text{CuFe}_2\text{O}_4 > \text{con-CuFe}_2\text{O}_4$, meso- $\text{CoFe}_2\text{O}_4 > \text{con-CoFe}_2\text{O}_4$), while CuFe_2O_4 was superior to CoFe_2O_4 . The persulfate successfully degrade organic pollutants over a wide pH range due to its high standard oxidation potential (2.6 V), which allowed easy activation to generate free sulfate radicals ($\text{SO}_4^{\cdot-}$) with a longer half-life. Fe^{3+} reduction by Cu^+ was thermodynamically favorable, which

benefitted the $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Cu}^+/\text{Cu}^{2+}$ redox cycles in meso- CuFe_2O_4 [120]. As shown in Fig. 9(a), a possible mechanism for persulfate activation by $\text{CuO-Fe}_3\text{O}_4$ was proposed. First, a Fenton-like reaction occurs between Cu(II) and $\text{S}_2\text{O}_8^{2-}$ at the surface of $\text{CuO-Fe}_3\text{O}_4$, associated with the formation of Cu(III) and $\text{SO}_4^{\cdot-}$, which might lead to the formation of $\text{HO}^{\cdot}$ radicals [117]. The $\text{CuO-Fe}_3\text{O}_4$ catalyst is relatively stable because it remained in the spinel crystalline form in the cubic phase at $\text{pH} = 11.0$. However, the reason for the gradually declining catalytic activity observed at $\text{pH} = 11.0$ is unclear.

Kalal et al. [121] prepared a copper pyrovanadate photo Fenton catalyst using a wet chemical method and applied it to the degradation of neutral red and azure B. The authors found that the photo Fenton activity of copper pyrovanadate was much higher than those of CuO and V_2O_5 . This enhanced efficiency was mainly due to the simultaneous activation of hydrogen peroxide in the presence of copper and vanadium.

5. Copper-based catalysts for solid waste remediation

Copper-based catalysts have also been intensively investigated in solid waste remediation and have shown promising performance. Soot particulates emitted from diesel engines have attracted much attention due to the serious damage they cause to the human body and environment [122]. Vehicle manufacturers have made good progress in eliminating soot from emissions. Currently, the combination of diesel particulate filters (DPFs) with soot oxidation catalysts is regarded as the most efficient after-treatment technology. Several copper ox-

Fig. 9. (a) Mechanism of persulfate activation by $\text{CuO-Fe}_3\text{O}_4$, adapted from Ref. [117]; SEM images of (b) meso- CuFe_2O_4 , (c) con- CuFe_2O_4 , (d) meso- CoFe_2O_4 , and (e) con- CoFe_2O_4 ; (f) Removal efficiency of imidacloprid using different catalysts; (g) Kinetic analysis of imidacloprid degradation ($\ln(C/C_0)$ vs. time); Adapted from Ref. [118].

ides, such as mixed oxides or perovskite-like oxides, have been shown to be effective for soot catalytic combustion.

It is difficult for soot particles to enter the inner pores of most catalysts with meso- or microporous structures because they usually possess a large diameter of more than 25 nm. Increasing the pore diameter to the macroscale can improve the soot combustion activity. Through the reasonable design of catalyst morphology, the catalytic activity for soot combustion can be efficiently improved. The morphological design of CuO arrays is important for the synthesis of highly efficient soot combustion catalysts to increase the contact efficiency between the catalysts and soot. Fig. 10(b) and (c) show good contact conditions between soot particles and CuO nanorods, similar to raindrops on a blade. The abundant space among loaded nanorods was also convenient for the transfer of reaction gases [123]. Lawn-like CuO-based nanorod array catalysts exhibited excellent performance for diesel soot combustion in gravitational contact mode (Fig. 10(d)) and the inverse structure catalyst, with CeO₂ supported on the CuO surface, efficiently inhibited the sintering of Cu species and maintained the existence of active sites at the interface.

Ce-based or Ce-Zr mixed-oxide-supported Cu oxide have also been used for soot oxidation. Sudarsanam et al. [124] designed CuO_x nanoparticle-decorated CeO₂ nanocubes with high catalytic performance in soot oxidation, as shown in Fig. 10(e)

and (f). The presence of a higher number of Ce³⁺ ions and abundant oxygen vacancies at the Cu_x-CeO₂ nano-interface was responsible for the catalytic performance achieved by CuO_x-CeO₂ heterogeneous nanocatalysts [125,126]. To further enhance the performance of Cu-Mn-Ce mixed oxides, Liang et al. [127] reported the interaction between copper and cerium, which greatly enhanced the rapid release of lattice oxygen in a reducing atmosphere due to the incorporation of Mn^{x+} into the CeO lattice.

Copper solid solution catalyst CuO/Ce_{0.8}Zr_{0.2}O₂ showed high catalytic activity due to its surface properties and the synergistic effect at the Cu-ceria interface [128,129]. The soot combustion rate at 400°C obtained using a copper/ceria-zirconia catalyst approached that of 1% Pt/Al₂O₃, making it a promising candidate for DPF catalysts with the benefit of lower cost compared with noble metals.

A Cu-based perovskite oxide catalyst has also been reported in soot oxidation. The porous structural characteristics of perovskite contribute to soot capture and catalytic performance in soot combustion, which is largely affected by the chemical composition, grain size, specific surface area, and pore structure [130]. Those structure features are directly related to the ion substitution ratio and calcination temperature [131]. Nanometric perovskite catalyst La_{1-x}K_xCo_{1-y}CuO_{3-σ} possesses high activity and a large amount of surface oxygen species (O²⁻ and

Fig. 10. (a, b) SEM images of the mixture of soot and nanorod array under gravitational contact mode (GCM); (c) Schematic illustration of the mechanism for lawn-like CuO-based nanorods array used for diesel soot combustion under GCM; (d) Derivative thermogravimetry (DTG) profiles of soot combustion, adapted from Ref. [123]; (e) Schematic diagram of the oxidation of diesel soot over CuO_x-decorated CeO₂ nanocubes; (f) Soot conversion vs. temperature under tight contact conditions, adapted from Ref. [124].

O²⁻), with more tetravalent cobalt ions and better reducibility than other catalysts, which resulted in its superior catalytic performance [132].

6. Conclusions and prospect

This review summarizes recent progress in copper-based non-precious metal heterogeneous catalysts for environmental remediation, focusing on the catalytic oxidation of carbon monoxide, the selective catalytic reduction (SCR) of NO_x using NH₃, the catalytic oxidation of VOCs, the catalytic degradation of organic pollutants, and the catalytic oxidation of soot. Copper oxides exhibited various functions in these heterogeneous catalytic reactions. CuO_x can serve as a model catalyst to better elucidate the origin of catalytic active sites and the mechanism of different catalytic reactions. The structure-activity relationship of Cu-based catalysts has been touched on to illustrate the general principle for the rational design of highly efficient catalysts. Supported CuO_x can effectively enlarge the surface area necessary for high CuO_x dispersion and engineer interfacial catalytic active sites to further improve the physical and/or chemical properties of the corresponding composite catalysts. Solid solution CuO_x-X composites are promising catalysts with unique atomic arrangements that can promote both the low-temperature activity and catalytic stability of CuO_x for applications under practical industrial conditions.

However, copper-based catalysts still suffer from many problems that inhibit their wide application that need to be addressed in future, as follows: (1) CuO_x nanoparticle aggregation: At higher Cu content in the catalyst, dispersed CuO small nanoparticles will aggregate to form large nanoparticles, accompanied by serious catalytic activity degradation; (2) Easily poisoned by SO₂ and moisture: SO₂ and moisture can poison Cu-zeolites by forming CuSO₃ at low temperatures (<200 °C), which can block the zeolite pores and/or cover the active sites; (3) Poor low-temperature catalytic activity: The development of active and stable copper based catalysts for low-temperature pollutant control remains a significant challenge.

To address these issues, a few design principles might guide the rational fabrication of effective Cu-based catalysts. The engineering of strong metal oxide-support interactions at the interface by controlling the morphology and facets could effectively prevent particle aggregation and the associated degradation of catalytic activity. To fabricate CuO_x catalysts with enhanced durability and strong resistance to H₂O and SO₂, the design of multiple active sites or trapping sites for H₂O and SO₂ could be emphasized. Engineering high index facets and high-energy interfacial structure that feature reversible oxidation capabilities could enhance the catalytic activity of CuO_x catalysts at low temperature. Furthermore, single-atom catalysts have shown excellent high specific activities with decreased metal particle sizes and maximized utilization of metallic materials. Therefore, a single-atom Cu catalyst would be an interesting and promising catalyst to explore. Although extensive effort has been devoted to address these problems, the limited progress should motivate increased attention toward tailoring these potential catalysts moving forward.

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Graphical Abstract

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Copper-based non-precious metal heterogeneous catalysts for environmental remediation

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This review presents a comprehensive discussion on recent progresses of copper-based non-precious metal heterogeneous catalysts for various environmental remediation reactions, as well as a detailed analysis of catalysts structure-reactivity relationship.

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铜基非贵金属异相催化剂在环境修复中的应用

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摘要: 近年来, 全球经济和工业高速发展带来的环境问题, 不仅严重影响着经济社会的可持续发展, 更极大地危害着人类健康. 石油化工、医药生产和交通运输等过程产生的气、液、固相污染物可直接或间接造成臭氧层空洞、光化学烟雾及水体污染等重大环境问题. 气相污染物中, CO和可挥发性有机物(VOCs)不仅具有生物毒性, 更是形成光化学烟雾等大气污染的主要前驱体. NO_x和SO₂会造成酸雨的形成, 极大地破坏生态系统. 工业废水中难分解的有机污染物可对环境造成持续性破坏. 而不完全燃烧产生的碳烟颗粒物不仅影响气候和大气环境, 同时可导致心血管疾病高发, 危害人体健康. 源头控制是环境污染治理的关键, 而催化净化是当前污染物源头控制最有效的技术之一. 因此, 设计和开发稳定、高效的环境修复催化剂是科学家们面临的一个关键问题. 传统贵金属(Pt, Rh, Pd)催化剂虽然催化活性高, 但是存在价格昂贵且易中毒等不足. 而过渡金属及其氧化物因具有高活性、价格低廉和高储量等特点有望成为贵金属的替代催化剂.

铜是具有3d轨道的过渡金属, 有活泼的物理化学性质, 是工业中大量应用的有色金属. 铜基氧化物因高氧化还原电势和低环境危害被广泛应用于热催化、电催化和光催化. 基于文献报道, 铜基催化剂主要分为三类: 铜氧化物(CuO_x), 负载型铜氧化物(CuO_x/support)和固溶体铜氧化物(CuO_x-X). 本篇综述首先探讨了铜氧化物的价态、晶体结构、形貌、暴露晶面以及载体与催化剂活性之间的内在联系, 阐明铜基催化剂结构与性能的构效关系及高效催化剂的设计原则; 继而全面总结了近年来不同类型的铜基材料在催化净化环境污染物中的应用, 主要介绍了以下5类反应: CO的催化氧化, NO_x的选择性催化还原(SCR), VOCs的完全燃烧, 废水中有机污染物降解, 以及碳烟颗粒物催化燃烧. 我们深入阐述铜氧化物的催化活性位点和催化机制; 分析负载型铜基催化剂的比表面积、分散度、协同作用和界面作用对催化剂的活性和稳定性的影响; 阐明固溶体催化剂的独特原子组成设计与性能关系, 为高效催化剂设计提供思路. 此外, 本综述对铜基催化剂在环境催化中的研究现状以及尚未解决的问题进行了剖析与展望. 通过铜氧化物表面调控, 复合催化剂的界面调控, 具有更高稳定性和抗中毒性的高效催化剂有望开发成功, 而团簇及单原子铜催化剂也有望在此领域有所突破.

关键词: 铜基催化剂; 异相催化; CO催化氧化; 选择性催化还原; 可挥发性有机物氧化; 有机污染物降解; 碳烟颗粒物催化燃烧

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