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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 CuO_x-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.

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 3*d* 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 NH_3, 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 (Cu_2O). 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

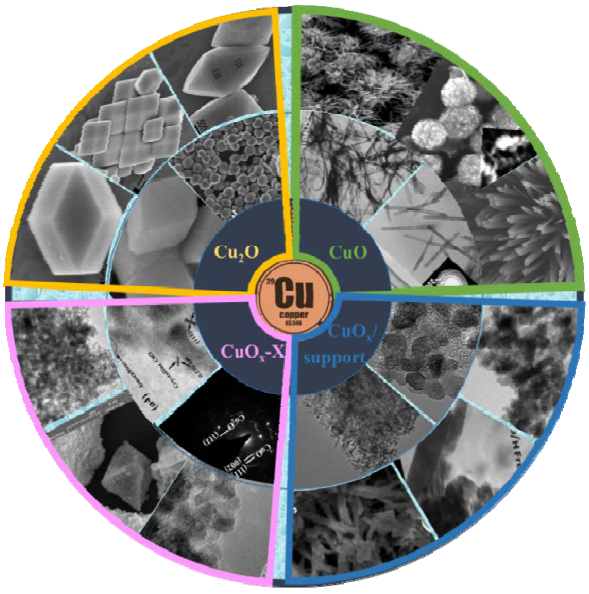

Fig. 1. Structures and morphologies of Cu_2O, CuO, supported CuO_x, and CuO_x-X catalysts.

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 ($Cu^{2+}\leftrightarrow Cu^{1+}$, $Cu^{1+}\leftrightarrow Cu^{0}$) or two-electron ($Cu^{2+}\leftrightarrow Cu^{0}$) pathways. Furthermore, different morphologies and crystalline structures of CuO and Cu_2O 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 (Cu_2O) 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]. Cu_2O has a face-centered cubic (*fcc*) crystal structure (space group, O^4_K-*pn3m*), in which oxygen atoms form