



Support-dependent active species formation for CuO catalysts: Leading to efficient pollutant degradation in alkaline conditions



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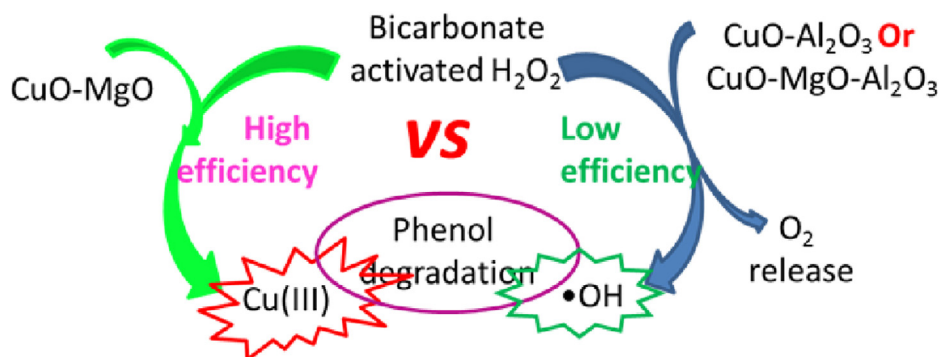
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HIGHLIGHTS

- The active species formation for degradation is controlled by supporting material.
- The Cu(III) species based degradation displays better efficiency than $\bullet\text{OH}$ in base.
- Redox metal oxide catalyst leaching can be controlled to a very low level in base.

GRAPHICAL ABSTRACT



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ABSTRACT

Redox metal ions play the crucial role in versatile advanced oxidation technologies, in which controlling the active species formation through catalyst design is one of the key challenges in oxidant utilization. This work describes an example of different active species formations in CuO-mediated degradation just because of supporting material differences. Although three CuO catalysts were prepared by similar procedures, it was found that CuO-MgO catalyst demonstrated high efficiency in phenol degradation with bicarbonate activated H₂O₂, in which the superoxide radical is crucial, while hydroxyl radical and singlet oxygen are ignorable. For the CuO-MgO-Al₂O₃ and CuO-Al₂O₃ catalysts, the degradation proceeds by popular hydroxyl radical based process, however, the efficiency was poor. The EPR experiments also confirmed the absence of hydroxyl radical in CuO-MgO system but its presence in CuO-MgO-Al₂O₃ and CuO-Al₂O₃ system. The high catalytic efficiency with ignorable hydroxyl radical in the CuO-MgO system leads us to propose that an alternative Cu(III) species dominates the degradation. The basic MgO support may facilitate the formation of the Cu(III) species, whereas the neutral MgO-Al₂O₃ and acidic Al₂O₃ supports

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are unable to stabilize the high valent Cu(III) species, leading to the common hydroxyl radical mechanism with low efficiency of H_2O_2 in alkaline conditions.

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1. Introduction

Wastewater treatment is a critical process for human beings to recycle polluted water from chemical related industries and living activity of human beings. Due to the low efficiencies like long treatment time and large space requirement with other biological limitations, traditionally biological technologies are apparently not enough to achieve the prompt treatment of wastewater which is rapidly increasing. Alternatively, versatile chemical technologies have provided great opportunities in pollutant degradation with high efficiency, and the advanced oxidation technologies are among the most attractive [1–4].

Fundamentally, two different degradation mechanisms were involved in various advanced oxidation technologies, including (1) hydroxyl radical ($\bullet\text{OH}$) based degradation in which $\bullet\text{OH}$, single oxygen ($^1\text{O}_2$) and superoxide radical ($\text{O}_2^{\bullet-}$) are generated in a chain process, and (2) high valent metal ions based degradation in which these high oxidation state metal ions directly oxidize versatile pollutants [2,5–10]. In fact, the degradation of pollutants by aerobic bacteria proceeds by the second mechanism [11]. While these mechanisms may simultaneously happen in one chemical process, the $\bullet\text{OH}$ radical based degradation generally dominates the H_2O_2 , ozone, photocatalysis and wet air oxidation related processes. Due that $\bullet\text{OH}$, $^1\text{O}_2$ and $\text{O}_2^{\bullet-}$ can interact with each other in a chain process to release O_2 [2], it apparently causes the increased oxidant cost in wastewater treatment, for example, in the case of using H_2O_2 as oxidant. On the other side, the high valent metal ion mediated degradation is generally more efficient in oxidant utilization, thus reduces the oxidant cost in a practical application. In particular, beside the drawback of short lifetime of oxide catalysts due to the metal leaching in wastewater treatment, the high cost of oxidants is another serious challenge which blocks the wide applications of advanced oxidation technologies. Therefore, exploring new catalysts for efficient oxidant utilization is still badly needed for their practical applications. Here, we demonstrate an example of that the formation of the active species for pollutant degradation can be controlled through catalyst preparation. As disclosed, in alkaline conditions, CuO-MgO catalyst degrades phenol through the plausible active Cu(III) species with high efficiency, whereas CuO-MgO- Al_2O_3 and CuO- Al_2O_3 catalysts proceed by common $\bullet\text{OH}$ radical based mechanism with low efficiency. Attractively, the alkaline treatment conditions can significantly inhibit the catalyst leaching, extend its lifetime with reduced cost, which may provide great opportunities for practical application.

2. Experimental section

2.1. Chemical and reagents

Phenol, 4-chlorophenol (4-CP), 2-chlorophenol (2-CP), 2,4-dichlorophenol (DCP), nitrobenzene, $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (>99%), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($\geq 99\%$), Na_2CO_3 ($\geq 99.8\%$), NaHCO_3 (99.5%), hydrogen peroxide (30%, w/w), NaOH (99.8%), magnesium oxide, sodium azide, isopropanol (IPA), benzoquinone (BQ), Na_2SO_4 , $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$ and other chemical were purchased from local Sinopharm Chemical Reagent, and were used without further purification.

2.2. Preparation of powdered catalyst by co-precipitation method

The powdered catalyst including CuO-MgO, CuO-MgO- Al_2O_3 , CuO- Al_2O_3 , MgO- Al_2O_3 were prepared in water bath at 60°C using a co-precipitation method. In a typical procedure, certain amount of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were completely dissolved in 100 mL of deionized water, then it was added into 100 mL of 0.3 M Na_2CO_3 solution drop by drop with stirring, and the pH of solution was controlled around pH 10 by adding aqueous solution of 2 M NaOH as needed. After that, the solution was continuously stirred at 60°C for another 1 h, and the resulting precipitate was aged for 24 h at room temperature, followed by filtering and washing with deionized water until the pH keeps constant. Then it was dried at 100°C for 12 h, followed by calcination in muffle furnace at 500°C for 6 h to obtain the powdered catalyst.

2.3. Preparation of powdered CuO@MgO catalyst by impregnation method

In a typical procedure, 0.49 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 10 mL of distilled water completely, then it was added into a 25 mL round bottom flask containing 2 g of MgO with stirring, followed by drying with rotary evaporation at 80°C . The obtained powder was dried overnight at 100°C in oven, then calcinated in muffle furnace at 500°C for 6 h to obtain the expected CuO@MgO catalyst.

2.4. Phenol degradation tests

Typically, 10 mg of catalyst with 0.025 g of NaHCO_3 were added into 20 mL of aqueous solution containing 0.5 mM phenol and 30 mM H_2O_2 . The resulting solution was stirred for 1 h at 45°C . Periodically, samples were withdrawn from the reaction solution, filtered through 0.22 μm filter, and immediately analyzed by high performance liquid chromatography (HPLC FL-2200) for phenol degradation, and by HACH-1010 for COD removal.

2.5. Quenching effect with different scavengers

Typically, isopropyl alcohol (IPA), sodium azide (NaN_3) and benzoquinone (BQ) were employed as scavengers for $\bullet\text{OH}$, $^1\text{O}_2$ and $\text{O}_2^{\bullet-}$, respectively. In a general procedure, 0.15 mL of IPA and 0.025 g of NaHCO_3 were added to 0.2 mL of aqueous solution containing 4700 mg/L phenol, which was next added to 6 mL aqueous solution containing 100 mM H_2O_2 with 10 mg of CuO-MgO catalyst. The resulting solution was then corrected to total 20 mL with deionized water, then stirred at 45°C for 1 h. During this period, periodically 2 mL of the reaction mixture were taken out at the given time intervals, filtered through 0.22 μm filter and immediately analyzed by high performance liquid chromatography (HPLC FL-2200) for phenol degradation.

2.6. Quenching effect by combination of different scavengers

In a typical procedure, 0.2 mL of aqueous solution containing 4700 mg/L phenol and 0.025 g of NaHCO_3 were added to 13.8 mL deionized water containing 6.5 mg of BQ and 13 mg of NaN_3 . Then, 6 mL of solution containing 100 mM H_2O_2 with 10 mg of CuO-MgO catalyst were added to above prepared solution, and stirred at 45°C

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