available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue on Environmental Catalysis and Materials)

Synergistic degradation of phenols by bimetallic CuO–Co₃O₄@ γ -Al₂O₃ catalyst in H₂O₂/HCO₃[–] system

Yibing Li ^{a,b}, Ali Jawad ^b, Aimal Khan ^b, Xiaoyan Lu ^b, Zhuqi Chen ^b, Weidong Liu ^{a,#}, Guochuan Yin ^{b,*}^a College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, Zhejiang, China^b Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, Hubei, China

ARTICLE INFO

Article history:

Received 26 March 2016

Accepted 29 March 2016

Published 5 June 2016

Keywords:

Synergistic effect

Phenol degradation

Copper/cobalt oxide catalyst

Mechanistic study

Bicarbonate-activated H₂O₂

ABSTRACT

The development of new catalytic techniques for wastewater treatment has long attracted much attention from industrial and academic communities. However, because of catalyst leaching during degradation, catalysts can be short lived, and therefore expensive, and unsuitable for use in wastewater treatment. In this work, we developed a bimetallic CuO–Co₃O₄@ γ -Al₂O₃ catalyst for phenol degradation with bicarbonate-activated H₂O₂. The weakly basic environment provided by the bicarbonate buffer greatly suppresses leaching of active Cu and Co metal ions from the catalyst. X-ray diffraction and X-ray photoelectron spectroscopy results showed interactions between Cu and Co ions in the CuO–Co₃O₄@ γ -Al₂O₃ catalyst, and these improve the catalytic activity in phenol degradation. Mechanistic studies using different radical scavengers showed that superoxide and hydroxyl radicals both played significant roles in phenol degradation, whereas singlet oxygen was less important.

© 2016, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

With the rapid development of the global economy, scarcity of clean water is becoming a major challenge for a sustainable society. Also, the increased amounts of wastewater produced as a result of expansion of industrial production are seriously affecting the environment and human health in developing countries. Various biological, physical, and chemical techniques have been developed and used for wastewater treatment [1–6]. Biological techniques are most popular because of their low cost and moderate treatment conditions. However, because of their long treatment times, large land requirements, and sensitivity to highly concentrated wastewater, current biological

techniques are inadequate for increasing wastewater treatment requirements. Chemical-based advanced oxidation techniques are more attractive than biological techniques because they require less land for treatment, can be used to treat low and high concentrations of pollutants, and, in particular, the treatment period is much shorter. However, these catalytic techniques have not been widely used in wastewater treatment, partly because, as the treatment proceeds, the formation of small organic acids can cause catalyst leaching, which increases the catalyst cost and can cause toxic heavy metal pollution. New concepts in catalyst design for wastewater treatment are therefore needed.

Recently, based on reports that bicarbonate (HCO₃[–])-acti-

* Corresponding author. Tel: +86-27-87543032; Fax: +86-27-87543632; E-mail: gyin@hust.edu.cn

Corresponding author. E-mail: Liuwd@zjnu.cn

This work was supported by the National Natural Science Foundation of China (21273086) and Chutian Scholar Foundation from Hubei Province, China.

DOI: 10.1016/S1872-2067(15)61092-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 6, June 2016

vated H_2O_2 can be used to oxidize various organic compounds [7], we developed an $\text{H}_2\text{O}_2/\text{HCO}_3^-$ system for wastewater treatment using aqueous Co and Mn catalysts. We also performed fixed-bed tests on supported Co catalysts, which showed that they had good catalytic efficiencies [8–12]. Similar $\text{H}_2\text{O}_2/\text{HCO}_3^-$ systems with different redox metal ions have also been extensively explored in other laboratories [13]. Compared with neutral to acidic advanced oxidations, the $\text{H}_2\text{O}_2/\text{HCO}_3^-$ system can activate H_2O_2 to generate perbcarbonate (HCO_4^-) as the oxidant in situ, and can also generate weakly basic buffer conditions; this inhibits wastewater acidification and effectively prevents catalyst leaching from the support. $\text{H}_2\text{O}_2/\text{HCO}_3^-$ systems have been used in persulfate-oxidant-mediated wastewater treatment [14]. Most previous studies of new pollutant treatments have been based on degradation catalyzed by mono-redox metal ions with an $\text{H}_2\text{O}_2/\text{HCO}_3^-$ system. Advanced oxidation techniques use heterogeneous redox catalysts consisting of supported redox metal ions, and many non-redox and redox metal ions have been widely used as additives to modify the reactivity and control the catalyst lifetime; however, their roles have not yet been fully elucidated [15,16]. Here, we introduce a bimetallic catalyst, $\text{CuO-Co}_3\text{O}_4@ \gamma\text{-Al}_2\text{O}_3$, for phenol degradation using an $\text{H}_2\text{O}_2/\text{HCO}_3^-$ system for wastewater treatment. A synergistic effect was observed.

2. Experimental

2.1. Chemicals and equipment

Phenol, 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), 4-chlorophenol (4-CP), nitrobenzene, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, NaHCO_3 , H_2O_2 (30%), sodium meta-aluminate, $\gamma\text{-Al}_2\text{O}_3$ (A-AP-60-p), Co_3O_4 , CuO, NaN_3 , isopropanol (IPA), benzoquinone (BQ), and other chemicals were purchased from Sinopharm Chemical Reagents, and were used without further purification. All sample solutions were prepared using deionized water. The chemical oxygen demand (COD) was measured using an HACH DR1010 instrument. The total organic carbon (TOC) was determined using a TOC analyzer (Analytikjena Multi N/C-3100). Metal ion leaching was detected using atomic absorption spectroscopy (AAS; Analyst 300, Perkin Elmer). X-ray diffraction (XRD) was performed using an X'Pert PRO instrument, and Fourier-transform infrared (FT-IR) spectroscopy was performed using a Bruker Equinox 55 instrument. Phenol degradation was monitored using a high-performance liquid chromatography (HPLC) system (FL2200) equipped with an ultraviolet detector and C_{18} column (250 mm $\times$ 4.6 mm). The flowing phase composition was methanol-water (60:40, v/v).

2.2. Preparation of $\text{Co}_3\text{O}_4@ \gamma\text{-Al}_2\text{O}_3$ catalyst

In a typical experiment, an aqueous solution (10 mL) containing $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.20 g, 0.7 mmol) was added dropwise with stirring to an aqueous solution (10 mL) containing NaAlO_2 (0.1 g, 1.2 mmol). The resulting solution was added to a 25 mL round-bottomed flask containing $\gamma\text{-Al}_2\text{O}_3$ (1 g), followed by

rotary evaporation at 80 °C. The obtained powder was dried overnight in an oven at 90 °C, and then calcined in a muffle furnace at 500 °C for 6 h to obtain the $\gamma\text{-Al}_2\text{O}_3$ -supported Co catalyst, denoted by $\text{Co}_3\text{O}_4@ \gamma\text{-Al}_2\text{O}_3$; AAS showed that it contained 1.6% Co. A $\gamma\text{-Al}_2\text{O}_3$ -supported Cu catalyst ($\text{CuO}@ \gamma\text{-Al}_2\text{O}_3$) was prepared using the same procedure; AAS showed that it contained 6.2% Cu.

2.3. Preparation of $\text{CuO-Co}_3\text{O}_4@ \gamma\text{-Al}_2\text{O}_3$ catalyst

In a typical procedure, an aqueous solution (10 mL) containing $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.12 g, 0.5 mmol) was added dropwise with stirring to an aqueous solution (10 mL) containing NaAlO_2 (0.05 g). The resulting mixture was added to a 25 mL round-bottomed flask containing $\text{Co}_3\text{O}_4@ \gamma\text{-Al}_2\text{O}_3$ (0.5 g, 0.7 mmol:1 g), followed by rotary evaporation at 80 °C. The obtained powder was dried overnight in an oven at 90 °C, and then calcined in a muffle furnace at 500 °C for 6 h to obtain the $\gamma\text{-Al}_2\text{O}_3$ -supported catalyst, denoted by $\text{CuO-Co}_3\text{O}_4@ \gamma\text{-Al}_2\text{O}_3$; AAS showed that it contained 1.5% Co and 5.5% Cu.

2.4. Preparation of $\text{CuO-Co}_3\text{O}_4$ catalyst by coprecipitation

An aqueous solution (20 mL) containing $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.24 g) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.40 g) was added dropwise with continuous stirring to an aqueous Na_2CO_3 solution (0.5 mol/L, 100 mL) at 60 °C. After stirring for 2 h, the black solution was allowed to cool, filtered, washed three times with deionized water, and then dried in a vacuum oven overnight at 50 °C. The dried black powder was calcined at 400 °C for 5 h to obtain a binary metal oxide, i.e., the $\text{CuO-Co}_3\text{O}_4$ catalyst.

2.5. Bench-test phenol degradation

In a typical experiment, an aqueous phenol solution (0.2 mL, 4700 mg/L), NaHCO_3 (0.025 g), 100 mmol/L H_2O_2 solution (10 mL), and $\text{CuCo}@ \gamma\text{-Al}_2\text{O}_3$ catalyst (10 mg) were added to a 25 mL glass bottle; the volume was made up to 20 mL with deionized water and the mixture was stirred at 45 °C for 1 h. At given time intervals, samples (2 mL) of the reaction mixture were removed and filtered through a 0.22 μm filter. Phenol degradation was determined by HPLC, and COD removal was measured.

2.6. Radical trapping by single scavenger

IPA (0.15 mL) was mixed with aqueous phenol solution (0.2 mL, 4700 mg/L), NaHCO_3 (0.025 g), 100 mmol/L H_2O_2 solution (10 mL), and $\text{CuO-Co}_3\text{O}_4@ \gamma\text{-Al}_2\text{O}_3$ catalyst (10 mg) in a 25 mL glass bottle. The volume was made up to 20 mL with deionized water and the solution was stirred at 45 °C for 1 h. At given time intervals, samples (2 mL) of the reaction mixture were removed and filtered through a 0.22 μm filter, and phenol degradation was immediately determined using HPLC.

2.7. Radical trapping by combination of different scavengers

An aqueous solution saturated with BQ (0.0065 g) and NaN_3

(0.20 g) was added to deionized water (9.8 mL) and mixed with an aqueous phenol solution (0.2 mL, 4700 mg/L), NaHCO_3 (0.025 g), 100 mmol/L H_2O_2 solution (10 mL), and $\text{CuO-Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$ catalyst (10 mg). The volume was made up to 20 mL with deionized water and the solution was stirred at 45 °C for 1 h. The inhibitory effects of the scavengers were investigated as follows. Sample (2 mL) of the solution was removed at given time intervals, filtered through a 0.22 μm filter, and phenol degradation was immediately determined using HPLC.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of the $\text{CuO-Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$ catalyst before and after reaction and those of the catalyst precursors, i.e., $\gamma\text{-Al}_2\text{O}_3$, $\text{Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$, and $\text{CuO}@\gamma\text{-Al}_2\text{O}_3$, are shown in Fig. 1. The XRD pattern of $\gamma\text{-Al}_2\text{O}_3$ had peaks at $2\theta = 67.1^\circ$, 37.2° , and 45.8° , corresponding to $\gamma\text{-Al}_2\text{O}_3$ [001-1308, 075-0921, and 034-0493], as reported in the reference [17]. The $\text{Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$ catalyst gave prominent peaks at $2\theta = 36.9^\circ$ and 31.1° and weak peaks at $2\theta = 45.0^\circ$, 55.5° , 59.2° , and 65° , corresponding to Co_3O_4 [082-2251] [17–19]. The XRD pattern of the $\text{CuO}@\gamma\text{-Al}_2\text{O}_3$ catalyst had two weak peaks at $2\theta = 35.5^\circ$ and 38.8° , corresponding to CuO [20]. The broadness and weak intensities of the CuO peaks for the $\text{CuO}@\gamma\text{-Al}_2\text{O}_3$ catalyst suggest that the Cu was highly dispersed, or incorporated into the Al_2O_3 skeleton. The XRD pattern of the fresh $\text{CuO-Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$ catalyst showed two major diffraction peaks at $2\theta = 35.6^\circ$ and 38.8° , attributed to pure CuO [041-0254] [20,21]. The XRD pattern of the $\text{CuO-Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$ catalyst after reaction was the same as that of the fresh catalyst, indicating that it had good stability during use. Notably, for the $\text{CuO-Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$ catalyst, the peak at $2\theta = 36.9^\circ$, corresponding to Co_3O_4 was weaker than that for the $\text{Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$ catalyst. The presence of Co_3O_4 in the $\text{CuO-Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$ catalyst increased the crystallinity of the CuO phase, as confirmed by the XRD analysis. In the $\text{CuO-Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$ catalyst, CuO probably surrounds Co_3O_4 , producing Cu–Co linkages, and these may be responsible for producing the synergistic effect and enhancing

Fig. 1. XRD patterns of $\gamma\text{-Al}_2\text{O}_3$ -supported catalysts after calcination.

the stability of $\text{CuO-Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$. In particular, the stronger CuO diffraction peaks in the $\text{CuO-Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$ catalyst and weaker Co_3O_4 peaks imply that CuO may surround Co_3O_4 sites; this is different from the highly dispersed CuO in the $\text{CuO}@\gamma\text{-Al}_2\text{O}_3$ catalyst. Such a structural change could be the origin of the improved synergistic pollutant degradation (vide infra).

The XPS spectra of $\text{Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$, $\text{CuO}@\gamma\text{-Al}_2\text{O}_3$, and $\text{CuO-Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$ before and after reaction were obtained to clarify the elementary states of Co and Cu in the solid catalysts; the spectra are shown in Fig. 2. According to the literature, the $\text{Co } 2p_{3/2}$ peak for metallic Co is observed at 778–779 eV, that for Co^{2+} is at 780–781 eV, with a strong satellite at 786–787 eV, and Co^{3+} gives a $\text{Co } 2p_{3/2}$ peak at 780–781 eV, without a satellite [22]. For $\text{Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$ and $\text{CuO-Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$, the $\text{Co } 2p_{3/2}$ and $2p_{1/2}$ levels were observed at 780.9 and 795.9 eV, respectively, with a weak satellite at 786.4 eV, confirming that Co^{2+} and Co^{3+} were present in the Co_3O_4 phase, as well as the species indicated by the XRD patterns [7,23]. In particular, although no variations in the binding energies were observed for $\text{Co } 2p_{3/2}$ in the $\text{Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$ and $\text{CuO-Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$ catalysts, the intensity of Co in $\text{CuO-Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$ was weaker because of the Cu coating on the Co_3O_4 site, as shown by the XRD analysis. Fig. 2(b) shows that the $\text{Cu } 2p$ core region for the $\text{CuO}@\gamma\text{-Al}_2\text{O}_3$ catalyst was split into two peaks, at binding energies of 934.7 eV ($\text{Cu } 2p_{3/2}$) and 954.5 eV ($\text{Cu } 2p_{1/2}$), and in-

Fig. 2. XPS spectra of Co 2p (a) and Cu 2p (b) core levels for $\text{Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$, $\text{CuO}@\gamma\text{-Al}_2\text{O}_3$, and $\text{CuO-Co}_3\text{O}_4@\gamma\text{-Al}_2\text{O}_3$ catalysts.

tense shakeup peaks were present. According to the literature, the peaks for metallic Cu and Cu₂O appear below 933 eV, with no shakeup peaks, and CuO typically shows binding energies higher than 933 eV (933.5–935.1 eV) along with a satellite peak [20,24]. The XPS results strongly suggest the presence of Cu²⁺ as a CuO phase; these results are consistent with the XRD results for CuO@ γ -Al₂O₃ [21,22]. A comparison of the CuO–Co₃O₄@ γ -Al₂O₃ and CuO@ γ -Al₂O₃ catalysts shows that the presence of Co slightly shifted the Cu 2p_{3/2} and Cu 2p_{1/2} peaks for the Cu²⁺ cation to 933.7 and 953.8 eV, respectively (Fig. 2(b)). Overall, the XPS results confirm the presence of the CuO phase in the CuO@ γ -Al₂O₃ and CuO–Co₃O₄@ γ -Al₂O₃ catalysts [25]. The Co and Cu XPS spectra of the CuO–Co₃O₄@ γ -Al₂O₃ catalyst were obtained to confirm the stability and changes in the states of the active sites; the spectra are shown in Fig. 2(a, b). Co and Cu appeared as Co²⁺/Co³⁺ and Cu²⁺ in the CuO–Co₃O₄@ γ -Al₂O₃ catalyst after the reaction, as they did before the reaction; this indicates good regeneration of the active sites during the reaction. Regeneration of the active sites in the CuO–Co₃O₄@ γ -Al₂O₃ catalyst may arise from the difference between the redox potentials of Cu and Co (Co³⁺/Co²⁺, E° = 1.18 V; Cu²⁺/Cu⁺, E° = 0.17 V). This difference between the redox potentials could lead to thermodynamically feasible redox reactions between the active sites, resulting in active site regeneration.

Figure 3 shows the FT-IR spectra of γ -Al₂O₃ and the γ -Al₂O₃-supported catalysts. All four catalysts have similar spectra, with minor differences. In the spectrum of γ -Al₂O₃, the band at 760 cm^{−1} is attributed to the Al–O–Al tetrahedron anti-symmetric stretching vibration, and the band at 583 cm^{−1} is assigned to the vibration of six-coordinated Al–O [26,27]. According to the literature, the weak bands at 1096, 1090, and 1097 cm^{−1} can be attributed to Al–O–M species [28]. Although the Co loading on the γ -Al₂O₃ support was low, the weak absorbance band at 663 cm^{−1} can be assigned to Co–O stretching of Co₃O₄ in the Co₃O₄@ γ -Al₂O₃ and CuO–Co₃O₄@ γ -Al₂O₃ catalysts [27], and the weak peak at 846 cm^{−1} is assigned to Cu–O stretching in the CuO–Co₃O₄@ γ -Al₂O₃ catalyst. Brunauer–Emmett–Teller (BET) analysis showed that γ -Al₂O₃ and the Co₃O₄@ γ -Al₂O₃ catalyst had very similar surface areas, i.e., 105

and 108 m²/g, respectively. Cu loading decreased the surface area to 10 m²/g. Even for the CuO–Co₃O₄@ γ -Al₂O₃ catalyst, the surface area was only 54 m²/g (Table 1). Similar low surface areas have been reported for other supported Cu catalysts [29,30].

3.2. Catalytic efficiency of the catalyst/HCO₃[−]/H₂O₂ system in phenol degradation

The phenolic structure is present in many organic chemicals, and the production of phenolic compounds has serious negative impacts on the environment, plants, animals, aquatic organisms, and human health [31,32]. Their elimination has therefore attracted considerable attention from industrial and academic communities. In this study, we used phenol as a model compound to test the catalytic activity of CuO–Co₃O₄@ γ -Al₂O₃ in phenolic compound degradation with bicarbonate-activated H₂O₂. Figure 4(a) shows the degradation efficiencies of various catalysts with the HCO₃[−]/H₂O₂ system under the optimum conditions. As shown in Fig. 4(a), the CuO–Co₃O₄@ γ -Al₂O₃ catalyst gave 90% phenol degradation in 1 h at 45 °C, but the CuO@ γ -Al₂O₃ catalyst gave low degradation (about 39%), and that achieved with the Co₃O₄@ γ -Al₂O₃ catalyst was even lower (only 14%). Significantly, using a combination of CuO@ γ -Al₂O₃ and Co₃O₄@ γ -Al₂O₃ only provided 70% phenol degradation under conditions identical to those used with the CuO–Co₃O₄@ γ -Al₂O₃ catalyst, clearly supporting a synergistic effect between Cu and Co in the CuO–Co₃O₄@ γ -Al₂O₃ catalyst during phenol degradation. The synergistic effect in the CuO–Co₃O₄@ γ -Al₂O₃ catalyst was further confirmed by testing CuO, Co₃O₄, their physical mixture, and a binary metal oxide (CuO–Co₃O₄) under the same experimental conditions. Co₃O₄, CuO, and their mixture gave low phenol degradations. CuO achieved only 32% removal, and Co₃O₄ gave only 23% degradation. A physical mixture of these oxides under identical conditions gave only 46% phenol degradation. The binary oxide of Cu and Co (CuO–Co₃O₄) gave 57% phenol degradation. The COD removal rates, shown in Fig. 4(b), also suggest that a synergistic effect occurs between Cu and Co in the CuO–Co₃O₄@ γ -Al₂O₃ catalyst; it achieved 51% COD removal, whereas CuO@ γ -Al₂O₃ and Co₃O₄@ γ -Al₂O₃ gave only 37% and 9.8% COD removal, respectively. Similarly, TOC removal by the CuO–Co₃O₄@ γ -Al₂O₃ catalyst was much higher than those by CuO@ γ -Al₂O₃ and Co₃O₄@ γ -Al₂O₃ (40.2% vs 28.5% and 5.7%, see Table 1). The XDR and XPS results for the CuO–Co₃O₄@ γ -Al₂O₃ catalyst also implied a synergistic effect; a new CuO phase is formed in the CuO–Co₃O₄@ γ -Al₂O₃ catalyst, whereas no such phase is present in the CuO@ γ -Al₂O₃ catalyst, because of high CuO dispersion (vide supra).

Synergistic effects have been widely observed in heterogeneous catalysis, but their origins are unclear [15,16]. Here, coating Cu on the Co sites in the CuO–Co₃O₄@ γ -Al₂O₃ catalyst may have changed their structures and affected their redox behavior in pollutant degradation. However, the mechanism by which such interactions improve the degradation efficiency is still unclear. We are currently using homogeneous models, which are more convenient for mechanistic studies, to investi-

Fig. 3. FT-IR spectra of prepared γ -Al₂O₃-supported catalysts.

Fig. 4. (a) Activities of various catalysts in phenol degradation: (A) $\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$, (B) $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$, (C) CuO , (D) Co_3O_4 , (E) $\text{CuO} + \text{Co}_3\text{O}_4$, (F) $\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3 + \text{CuO}/\gamma\text{-Al}_2\text{O}_3$, (G) $\text{CuO}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$, (H) $\text{CuO}-\text{Co}_3\text{O}_4$; (b) COD removal by various catalysts; (c) Phenol degradation under various conditions: (1) $\text{CuO}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3 + \text{H}_2\text{O}_2 + \text{HCO}_3^-$, (2) $\text{CuO}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3 + \text{H}_2\text{O}_2$, (3) only H_2O_2 , (4) $\text{CuO}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3 + \text{HCO}_3^-$, (5) $\text{CuO}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$, (6) $\text{H}_2\text{O}_2 + \text{HCO}_3^-$, (7) leached Cu 0.6 ppm + $\text{H}_2\text{O}_2 + \text{HCO}_3^-$. Reaction conditions: phenol 0.5 mmol/L, NaHCO_3 15 mmol/L, H_2O_2 50 mmol/L, catalyst 10 mg, 45 °C, 1 h, CuO and Co_3O_4 3 mg.

gate how these additives affect the redox behavior of catalysts. The available data indicate that interactions of non-redox Lewis acids with redox metal ions may positively shift their redox potentials; this improves their electron-transfer abilities and affects their catalytic efficiencies in hydrogen abstraction and oxygen transfer [33–36]. Further research in this field may provide clear results that elucidate the origins of this synergistic effect. Figure 4(c) shows that in control experiments H_2O_2 and the $\text{CuO}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ or $\text{CuO}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst with bicarbonate showed no activity in phenol degradation, indicating that phenol adsorption on the $\gamma\text{-Al}_2\text{O}_3$ support was negligible. Although H_2O_2 alone is nearly inactive, bicarbonate addition to H_2O_2 leads to slow phenol degradation, as a result of the formation of percarbonate (HCO_4^-), which is also a strong oxidant [13]. Without bicarbonate, $\text{CuO}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3/\text{H}_2\text{O}_2$ showed good activity in phenol degradation, providing 72.4% phenol degradation in 1 h, and $\text{CuO}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3/\text{HCO}_3^-/\text{H}_2\text{O}_2$ achieved 90% phenol degradation, showing that it has the highest catalytic activity. Catalyst leaching is always a major challenge in pollutant treatment. It not only leads to high costs because of the reduced catalyst lifetime, but also potentially leads to toxic heavy metal pollution. We investigated leaching of the active catalyst components (Co and Cu); the results are shown in Table 1.

No detectable Co and only 0.6 ppm Cu leaching were observed for the $\text{CuO}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst; this is lower than the Cu leaching (0.75 ppm) for the $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst. The lower leaching can be attributed to two factors: (1) the weakly

basic environment generated by bicarbonate, which prevents acid dissolution of the catalyst, and (2) possible improved stability of the bimetallic $\text{CuO}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst. To verify whether the leached Cu ions contribute significantly to phenol degradation, 0.6 ppm of $\text{Cu}(\text{NO}_3)_2$ were used as the catalyst instead of $\text{CuO}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$. Phenol degradation was only 18.9%, and the COD removal (10%) was also far lower than that achieved using the $\text{CuO}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst. It is worth emphasizing that 0.6 ppm of leached Cu gradually accumulated during degradation, therefore the contribution of leached Cu from the $\text{CuO}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst must be lower than 0.6 ppm, i.e., the amount added at the beginning. In complementary degradation tests, other phenolic compounds, namely 4-CP, 2,4-DCP, 2,4,6-TCP, and nitrobenzene were investigated in complementary degradation tests. Figure 5 shows that 4-CP and 2,4,6-TCP were smoothly degraded, with nearly 100% conversion, 2,4-DCP degradation was greater than 90%, and 55% degradation of nitrobenzene, which is very robust, was achieved in 1 h. These results show the high catalytic efficiency of the $\text{CuO}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst in phenolic compound degradation; the COD and TOC removals confirm this.

Fig. 5. Degradation of substituted phenols with $\text{CuO}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst. Reaction conditions: substituted phenol 50 ppm, NaHCO_3 15 mmol/L, H_2O_2 50 mmol/L, catalyst 10 mg, 45 °C, 1 h.

Table 1
Effects of Co/Cu on catalytic activity.

Catalyst	S_{BET} (m^2/g)	Leaching (ppm)		Phenol removal (%)	COD removal (%)	TOC removal (%)
		Co	Cu			
$\gamma\text{-Al}_2\text{O}_3$	108	—	—	3.2	—	—
$\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$	105	0.08	—	14.2	9.8	5.7
$\text{CuO}/\gamma\text{-Al}_2\text{O}_3$	10	—	0.75	39.0	37.0	28.5
$\text{CuO}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$	54	—	0.60	90.0	51.0	40.2

The effects of various operating parameters, namely the Co and Cu loadings, calcination temperature, reaction temperature, and amounts of H_2O_2 and bicarbonate were also investigated to explain the efficiency of the BAP system using the $\text{CuO-Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst for phenol degradation. The efficiency of $\text{CuO-Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ calcined at 400 °C was better than those calcined at other temperatures; it gave 100% phenol degradation at 45 °C. However, at lower temperatures (25–30 °C), the degradation efficiency was poorer. In addition, phenol degradation increased with increasing amount of H_2O_2 and reached 100% after 1 h with 60 mmol/L H_2O_2 ; degradation also increased smoothly with increasing bicarbonate concentration (15–30 mmol/L). This trend clearly suggests that bicarbonate participates in the production of reactive oxygen species, which are believed to play the main role in the degradation process (vide infra).

3.3. Mechanistic studies

Free radicals and high-valent metal oxo species have been proposed as the active species in organic pollutant degradation, and they can concurrently occur in one catalytic system. In the present study, bicarbonate at a low concentration (15 mmol/L) was used to activate H_2O_2 and generate a weakly basic buffer environment in phenol degradation. However, it has also been reported that carbonate or bicarbonate can competitively react with $\cdot\text{OH}$ radicals, as shown in Eqs. (1) and (2), and this may retard degradation [37].

Various chemical scavengers have been used to trap these radicals in pollutant treatments [13]. Coumarin is widely used to detect $\cdot\text{OH}$ radicals in photoluminescence experiments [38]. In the presence of $\cdot\text{OH}$ radicals, 7-hydroxycoumarin can be generated by radical attack on coumarin, providing a strong fluorescence signal that indicates the presence of $\cdot\text{OH}$ radicals in solution. Figure 6 shows that in the presence of the $\text{CuO-Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst, H_2O_2 , HCO_3^- , and coumarin, a high-intensity fluorescence signal was immediately observed, indicating the presence of $\cdot\text{OH}$ radicals in the reaction solution. Phenol addition to the system slightly reduced the fluorescence intensity, suggesting that the phenol substrate may consume a certain amount of $\cdot\text{OH}$ radicals; however, its reaction rate with $\cdot\text{OH}$ radicals is much slower than that of coumarin. The addition of IPA, a widely used scavenger of $\cdot\text{OH}$ radicals [39], to the solution completely quenched the fluorescence signal, indicating complete trapping of $\cdot\text{OH}$ radicals by IPA. It is worth mentioning that although IPA addition can completely quench the fluorescence signal, it does not completely quench degradation. The presence of 0.1 mol/L IPA caused phenol degradation to drop from 90% to 70%, and it dropped to 60% with 0.5 mol/L IPA. The degradation efficiency was further reduced, to 50%, by adding 1 mol/L IPA. However, the effect of adding 2 mol/L IPA was the same as that of adding 1 mol/L IPA, indicating that about 50% of the degradation could be attributed to $\cdot\text{OH}$ or related radicals. BQ is a well-known superoxide radical ($\cdot\text{O}_2^-$) scavenger in pollutant treatment [40]. Here, BQ addition did

Fig. 6. Fluorescence tests with coumarin under various conditions. (1) Cat. + H_2O_2 + HCO_3^- + coumarin; (2) Cat. + H_2O_2 + HCO_3^- + phenol + coumarin; (3) Cat. + H_2O_2 + HCO_3^- + phenol + IPA + coumarin; (4) Cat. + H_2O_2 + HCO_3^- + phenol + NaN_3 + coumarin; (5) Cat. + H_2O_2 + HCO_3^- + phenol + IPA + NaN_3 + coumarin; (6) Cat. + H_2O_2 + coumarin; (7) Cat. + HCO_3^- + coumarin; (8) H_2O_2 + HCO_3^- + coumarin; (9) Cat. + coumarin; (10) coumarin. Reaction conditions: phenol 0.5 mmol/L, NaHCO_3 15 mmol/L, H_2O_2 50 mmol/L, catalyst 10 mg, 45 °C, 1 h.

not retard degradation, but the system was not as sensitive to BQ as to IPA. The presence of 2 mmol/L BQ caused degradation to drop from 90% to 67%, and 3 mmol/L BQ further reduced the efficiency slightly, to 63%. NaN_3 is a scavenger of singlet oxygen ($^1\text{O}_2$) [13]; it has been reported that NaN_3 could also react with $\cdot\text{OH}$ radicals (Eqs. (3) and (4)) [41], and the reaction rates are comparable (2×10^9 vs $1 \times 10^{10} \text{ (mol/L)}^{-1} \text{ s}^{-1}$). The presence of 5 mmol/L NaN_3 substantially reduced the degradation efficiency from 90% to 58%, and adding more NaN_3 did not further inhibit the reaction.

The inhibitory effects of combinations of different scavengers were further investigated; the results are shown in Fig. 7. A combination of BQ and NaN_3 can completely quench degradation in the first 0.5 h, with minor degradation in the next 0.5 h. This is similar to the effect of a combination of BQ and IPA. As described above, NaN_3 can quench both $^1\text{O}_2$ and $\cdot\text{OH}$ radicals, and the rate for $\cdot\text{OH}$ radical quenching is five times faster than that for $^1\text{O}_2$. The inhibitory effect of BQ plus NaN_3 is almost identical to that of BQ plus IPA, which quenches $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals, but not related $^1\text{O}_2$; this implies that $^1\text{O}_2$ may not play a significant role in this system. However, NaN_3 plus IPA can reduce degradation from 90% to 23%, but does not completely quench it, unlike BQ plus NaN_3 or IPA, indicating that there are $\cdot\text{O}_2^-$ radicals in the system and they are partly responsible for degradation. More importantly, if the suggestion that the role of $^1\text{O}_2$ in degradation in this system can be ignored is correct, the contributions from $\cdot\text{OH}$ radicals and related species will provide the major contribution to degradation. It has been reported that bicarbonate and/or carbonate can competitively react with $\cdot\text{OH}$ radicals, and serve as its scavenger, but the generated carbonate radical ($\text{CO}_3^{\cdot-}$) is also a powerful oxidant. Hoffman et al. [42] reported that the effect of bicarbonate ions on the rate of ultrasonic decomposition of methyl *tert*-butyl ether is negligible above bicarbonate concentrations of 1–2 mmol/L, and

Fig. 7. Inhibitory effects of scavenger combinations on phenol degradation. (1) No scavenger; (2) 3 mmol/L BQ + 15 mmol/L NaN₃; (3) 3 mmol/L BQ + 0.1 mol/L IPA; (4) 15 mmol/L NaN₃ + 0.1 mol/L IPA; (5) 3 mmol/L BQ + 0.1 mol/L IPA + 15 mmol/L NaN₃. Reaction conditions: phenol 0.5 mmol/L, NaHCO₃ 15 mmol/L, H₂O₂ 50 mmol/L, catalyst 10 mg, 45 °C, 1 h.

proposed that bicarbonate radicals can abstract hydrogen atoms from methyl *tert*-butyl ether. Here, carbonate radicals may similarly play a significant role in phenol degradation.

4. Conclusions

We showed that a system consisting of bicarbonate-activated H₂O₂ as the oxidant and a CuO–Co₃O₄@γ-Al₂O₃ catalyst can efficiently degrade phenolic compounds. A synergistic effect was observed in pollutant degradation. The results showed that this synergistic effect originated from interaction of active sites (CuO and Co₃O₄) in CuO–Co₃O₄@γ-Al₂O₃. Because of the weakly basic environment provided by bicarbonate and the interactions of Cu and Co in the CuO–Co₃O₄@γ-Al₂O₃ catalyst, Co leaching is negligible, and Cu leaching is limited to 0.6 ppm. Radical trapping tests using various scavengers revealed that $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals both play significant roles in pollutant degradation, but ${}^1\text{O}_2$ is less important. The efficient catalytic system for pollutant degradation developed in this study, using a base and a catalyst with a bimetallic synergistic effect, will help in the design of efficient catalysts that do not suffer from leaching, and has potential practical applications in various wastewater treatments.

Acknowledgments

The authors thank the Analytical and Testing Center of Huazhong University of Science and Technology for help in XRD and XPS analysis.

References

- [1] N. Oturan, M. Panizza, M. A. Oturan, *J. Phys. Chem. A*, **2009**, 113, 10988–10993.
- [2] M. Farhadian, D. Duches, C. Vachelard, C. Larroche, *Appl. Biochem. Biotechnol.*, **2008**, 151, 295–306.
- [3] L. G. Devi, G. Krishnamurthy, *J. Phys. Chem. A*, **2011**, 115, 460–469.
- [4] N. Oturan, M. H. Zhou, M. A. Oturan, *J. Phys. Chem. A*, **2010**, 114, 10605–10611.
- [5] S. Zhang, H. Zhao, in: M. Duke, D. Y. Zhao, R. Semiat eds., *Functional Nanostructured Materials and Membranes for Water Treatment*, Wiley, **2013**, 335.
- [6] P. Forde, C. Kennelly, S. Gerrity, G. Collins, E. Clifford, *Environ. Technol.*, **2015**, 36, 1188–1204.
- [7] A. H. Xu, H. Xiong, G. C. Yin, *J. Phys. Chem. A*, **2009**, 113, 12243–12248.
- [8] A. Jawad, Y. B. Li, X. Y. Lu, Z. Q. Chen, W. D. Liu, G. C. Yin, *J. Hazard. Mater.*, **2015**, 289, 165–173.
- [9] X. X. Li, Z. D. Xiong, X. C. Ruan, D. S. Xia, Q. F. Zeng, A. H. Xu, *Appl. Catal. A*, **2012**, 411–412, 24–30.
- [10] A. H. Xu, X. X. Li, S. Ye, G. C. Yin, Q. F. Zeng, *Appl. Catal. B*, **2011**, 102, 37–43.
- [11] Z. Yang, H. Wang, M. Chen, M. X. Luo, D. S. Xia, A. H. Xu, Q. F. Zeng, *Ind. Eng. Chem. Res.*, **2012**, 51, 11104–11111.
- [12] L. Zhou, W. Song, Z. Q. Chen, G. C. Yin, *Environ. Sci. Technol.*, **2013**, 47, 3833–3839.
- [13] S. X. Liang, L. X. Zhao, B. T. Zhang, J. M. Lin, *J. Phys. Chem. A*, **2008**, 112, 618–623.
- [14] Y. Lei, C. S. Chen, Y. J. Tu, Y. H. Huang, H. Zhang, *Environ. Sci. Technol.*, **2015**, 49, 6838–6845.
- [15] T. C. An, H. Yang, W. H. Song, G. Y. Li, H. Y. Luo, *J. Phys. Chem. A*, **2010**, 114, 2569–2575.
- [16] R. Hernandez, M. Zappi, J. Colucci, R. Jones, *J. Hazard. Mater.*, **2002**, 92, 33–50.
- [17] I. Zacharaki, C. G. Kontoyannis, S. Boghosian, A. Lycourghiotis, C. Kordulis, *Catal. Today*, **2009**, 143, 38–44.
- [18] B. Solsona, T. E. Davies, T. Garcia, I. Vázquez, A. Dejoz, S. H. Taylor, *Appl. Catal. B*, **2008**, 84, 176–184.
- [19] Y. H. Zhang, H. F. Xiong, K. Liew, J. L. Li, *J. Mol. Catal. A*, **2005**, 237, 172–181.
- [20] F. E. López-Suárez, A. Bueno-López, M. J. Illán-Gómez, *Appl. Catal. B*, **2008**, 84, 651–658.
- [21] B. R. Strohmeier, D. E. Levden, R. S. Field, D. M. Hercules, *J. Catal.*, **1985**, 94, 514–530.
- [22] Z. Ferencz, A. Erdohelyi, K. Baán, A. Oszkó, L. Óvári, Z. Kónya, C. Papp, H. P. Steinrück, J. Kiss, *ACS Catal.*, **2014**, 4, 1205–1218.
- [23] Z. Zsoldos, L. Guzzi, *J. Phys. Chem.*, **1992**, 96, 9393–9400.
- [24] G. Fierro, M. L. Jacono, M. Inversi, R. Dragone, P. Porta, *Top. Catal.*, **2000**, 10, 39–48.
- [25] P. W. Park, J. S. Ledford, *Appl. Catal. B*, **1998**, 15, 221–231.
- [26] S. Chaliha, K. G. Bhattacharyya, *J. Hazard. Mater.*, **2008**, 150, 728–736.
- [27] J. B. d'Espinose de la Caillerie, M. Kermarec, O. Clause, *J. Am. Chem. Soc.*, **1995**, 117, 11471–11481.
- [28] P. Shukla, H. Q. Sun, S. B. Wang, H. M. Ang, M. O. Tadé, *Sep. Purif. Technol.*, **2011**, 77, 230–236.
- [29] A. Alejandre, F. Medina, A. Fortuny, P. Salagre, J. E. Sueiras, *Appl. Catal. B*, **1998**, 16, 53–67.
- [30] V. Rives, A. Dubey, S. Kannan, *Phys. Chem. Chem. Phys.*, **2001**, 3, 4826–4836.
- [31] J. Garcia-Ivars, M. I. Iborra-Clar, M. I. Alcaina-Miranda, J. A. Mendoza-Roca, L. Pastor-Alcañiz, *J. Hazard. Mater.*, **2015**, 290, 51–59.
- [32] H. S. Park, J. R. Koduru, K. H. Choo, B. Lee, *J. Hazard. Mater.*, **2015**, 286, 315–324.
- [33] Z. Q. Chen, L. Yang, C. Choe, Z. A. Lv, G. C. Yin, *Chem. Commun.*, **2015**, 51, 1874–1877.

Graphical Abstract

Chin. J. Catal., 2016, 37: 963–970 doi: 10.1016/S1872-2067(15)61092-0

Synergistic degradation of phenols by bimetallic CuO–Co₃O₄@ γ -Al₂O₃ catalyst in H₂O₂/HCO₃[–] system

Yibing Li, Ali Jawad, Aimal Khan, Xiaoyan Lu, Zhuqi Chen, Weidong Liu*, Guochuan Yin*
Zhejiang Normal University; Huazhong University of Science and Technology

The synergistic effect was observed in CuO–Co₃O₄/Al₂O₃ catalyzed phenol degradation with H₂O₂/HCO₃[–] system, and the leachings of the active Cu and Co were greatly compressed due to the weak basic environment provided by bicarbonate buffer.

- [34] C. Choe, L. Yang, Z. A. Lv, W. L. Mo, Z. Q. Chen, G. X. Li, G. C. Yin, *Dalton Trans.*, **2015**, 44, 9182–9192.
[35] L. Dong, Y. J. Wang, Y. Z. Lv, Z. Q. Chen, F. M. Mei, H. Xiong, G. C. Yin, *Inorg. Chem.*, **2013**, 52, 5418–5427.
[36] H. J. Guo, Z. Q. Chen, F. M. Mei, D. J. Zhu, H. Xiong, G. C. Yin, *Chem. Asian J.*, **2013**, 8, 888–891.
[37] A. Jawad, X. Y. Lu, Z. Q. Chen, G. C. Yin, *J. Phys. Chem. A*, **2014**, 118, 10028–10035.
[38] Q. J. Xiang, J. G. Yu, P. K. Wong, *J. Colloid Interface Sci.*, **2011**, 357,

- 163–167.
[39] K. A. Hislop, J. R. Bolton, *Environ. Sci. Technol.*, **1999**, 33, 3119–3126.
[40] P. Raja, A. Bozzi, H. Mansilla, J. Kiwi, *J. Photochem. Photobiol. A*, **2005**, 169, 271–278.
[41] R. Zhao, J. Lind, G. Merenyi, T. E. Eriksen, *J. Am. Chem. Soc.*, **1994**, 116, 12010–12015.
[42] H. M. Hung, J. W. Kang, M. R. Hoffmann, *Water Environ. Res.*, **2002**, 74, 545–556.

负载型铜钴氧化物协同催化 H₂O₂/HCO₃[–] 降解苯酚

李一冰^{a,b}, Ali Jawad^b, Aimal Khan^b, 卢小艳^b, 陈朱琦^b, 刘卫东^{a,#}, 尹国川^{b,*}

^a浙江师范大学化学与生命科学学院, 浙江金华 321004

^b华中科技大学化学与化工学院, 湖北武汉 430074

摘要: 近年来, 环境污染特别是水的严重污染使其治理成为一个极具挑战性的课题. 各种污染物复杂的化学成分和催化剂在处理过程中的浸出、寿命及成本等问题是导致众多氧化催化剂难以实际应用的主要原因. 相对而言, H₂O₂ 是一种活性氧含量高、清洁并可在温和条件下使用的氧化剂, 在各种高级氧化技术中受到广泛关注. 而碳酸氢盐是一种弱碱性物质, 在自然界及水体系中广泛存在, 且无明显毒害. 它可活化 H₂O₂, 加快其氧化各种有机物, 并在废水处理领域开始受到关注. 该体系的明显优势在于处理体系始终处于微碱性环境, 可以有效避免金属氧化物催化剂在处理过程中由于体系酸化而带来的催化剂流失, 从而延长催化剂寿命, 降低催化剂成本.

本文采用浸渍法制备了一种双金属铜、钴氧化物催化剂及相关的对照催化剂体系, 利用碳酸氢盐活化 H₂O₂ 用于降解苯酚模拟废水. 通过各种空白实验发现, 负载于 γ -Al₂O₃ 表面的钴、铜氧化物催化剂 CuO–Co₃O₄@ γ -Al₂O₃ 具有最好的催化降解活性, 而 CuO@ γ -Al₂O₃, Co₃O₄@ γ -Al₂O₃, CuO–Co₃O₄ 及 CuO 和 Co₃O₄ 的物理混合物均表现出较差的催化性能. 由此可见, 在 CuO–Co₃O₄@ γ -Al₂O₃ 催化剂中, 铜、钴离子在苯酚降解过程中存在协同效应, 这可能与催化剂中钴、铜金属离子的相互作用相关. X 射线衍射和 X 射线光电子能谱结果表明, 反应前后 CuO–Co₃O₄@ γ -Al₂O₃ 催化剂中金属的氧化状态并未发生改变, 在使用过程中钴离子的浸出率可以忽略, 铜离子的浸出率也仅有 0.6 ppm. 荧光分析实验和自由基捕获实验表明, 只有添加 $\cdot$ O₂[–] 和 $\cdot$ OH 的捕获剂能明显抑制降解反应, 因而推测该反应体系对有机物的降解是一个自由基氧化过程, 起关键作用的可能是 $\cdot$ O₂[–] 和 $\cdot$ OH.

关键词: 协同效应; 苯酚降解; 铜/钴氧化物催化剂; 机理研究; 碳酸氢盐活化的过氧化氢

收稿日期: 2016-03-26. 接受日期: 2016-03-29. 出版日期: 2016-06-05.

*通讯联系人. 电话: (027)87543032; 传真: (027)87543632; 电子信箱: gyin@hust.edu.cn

#通讯联系人. 电子信箱: Liuwd@zjnu.cn

基金来源: 国家自然科学基金 (20921092, 21227801); 湖北省楚天学者基金.

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18722067>).