



Wet peroxide oxidation process catalyzed by Cu/Al₂O₃: phenol degradation and Cu²⁺ dissolution behavior

Wumin Zhang¹ · Huimin Zhuang² · Yu Guo¹ · Hua Chi¹ · Qiuyue Ding³ · Lu Wang¹ · Yanyan Xi^{1,4} · Xufeng Lin^{1,5}

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Abstract

Catalytic wet peroxide oxidation (CWPO) has become an important deep oxidation technology for organics removal in wastewater treatments. Supported Cu-based catalysts belong to an important type of CWPO catalyst. In this paper, two Cu catalysts, namely, Cu/Al₂O₃-air and Cu/Al₂O₃-H₂ were prepared and evaluated through catalytic degradation of phenol. It was found that Cu/Al₂O₃-H₂ had an excellent catalytic performance (TOC removal rate reaching 96%) and less metal dissolution than the Cu/Al₂O₃-air case. Moreover, when the organic removal rate was promoted at a higher temperature, the metal dissolution amounts was decreased. Combined with hydroxyl radical quenching experiments, a catalytic oxidation mechanism was proposed to explain the above-mentioned interesting behaviors of the Cu/Al₂O₃-H₂ catalyst for CWPO. The catalytic test results as well as the proposed mechanism can provide better guide for design and synthesis of good CWPO catalysts.

Keywords Catalytic wet peroxide oxidation · Supported Cu catalysts · Metal dissolution · Phenol oxidation · Reaction mechanism

Introduction

Water is the basic resource for all living things on earth, however, nowadays water shortage and pollution become increasingly serious problems for humankind. The improperly treated sewage discharged from plants is one of the main reasons responsible for water pollution. Therefore,

degradation of pollutants in wastewater has developed to be an important research field for reducing damage to water environment. Advanced oxidation processes (AOPs), known as a deep oxidation technology, take the advantage of oxidants that can produce highly reactive free radicals (such as ·OH, SO₄^{·-}) to oxidize organic contaminants in water. They are especially useful for the aqueous contaminants that are difficult to degrade with biologic methods. In particular, the ·OH radical does not introduce elements other than H and O into water, which fits the green chemistry idea for water treatment. For this goal, the AOP techniques using oxidants that can generate ·OH radicals, such as H₂O₂, O₃, and molecular O₂ (pure O₂ or air) etc (Li et al. 2019; Fu et al. 2020; Baloyi et al. 2018) are preferred over other oxidants like S₂O₈²⁻. O₂ is generally used under high pressures and temperatures, and the cost of O₃ is obviously higher than the other two oxidants. For example, Fu et al. (Fu et al. 2021) prepared Zn-CNTs-Cu composite for in situ generation of H₂O₂ to degrade 4-chlorophenol under 0.50 MPa (O₂) at 150 °C. MnCeO_x catalysts were prepared and used for the catalytic wet air oxidation of phenol at 2 MPa (O₂) (Geng et al. 2020).

Compared to O₂, H₂O₂ can degrade organic substances at lower temperatures and ambient pressure. For example, Jiao et al. reported that H₂O₂-driven Fenton-like treatment was

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✉ Xufeng Lin
hatrick2009@upc.edu.cn

¹ College of Chemistry and Chemical Engineering, China University of Petroleum (East China), Qingdao 266580, People's Republic of China

² Shandong Yellow Sea Institute of Science and Technology Innovation, Rizhao 276808, People's Republic of China

³ College of Material Science and Engineering, China University of Petroleum (East China), Qingdao 266580, People's Republic of China

⁴ Advanced Chemical Engineering and Energy Materials Research Center, China University of Petroleum (East China), Qingdao 266580, People's Republic of China

⁵ State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), Qingdao 266580, People's Republic of China

used for oxidation of 4-nitrophenol and Rhodamine B at the temperatures of ≤ 50 °C (Jiao et al. 2018).

It is undoubtedly essential to use catalysts to remove organic matters quickly and thoroughly in this progress, known as catalytic wet peroxide oxidation (CWPO). CWPO catalysts can be divided into homogeneous and heterogeneous ones in general, and the latter are more suitable for industrial applications due to their easier separation from solution. In particular, supported metal catalysts are widely applied due to high metal dispersion and therefore high catalytic activity become a research hot spot (Devlin and Harris 1984; Li et al. 2020; Wang and Tang 2021). Copper (Cu) is one of the commonly used active metals components, being lower cost compared to noble metals and higher activity compared to rare-earth metals. (Liu et al. 2022; Cui et al. 2022; Kumar et al. 2020; Jiang et al. 2022).

During the AOPs process, metal ions dissolution from supported catalysts into water can lead to second-time pollutions and thus increase the cost of post-treatment. Therefore, study on metal dissolution rules has an obvious practical significance. The dissolution of metal ions into water can be accelerated by short-chain acids, like maleic, formic and acetic acids, generated during CWPO process. And compared with the high calcination temperature (900 °C), the low temperature (500 °C) promotes the dissolution of Cu^{2+} into water (Brussino et al. 2019). Cu^{2+} dissolution occurs not only in CWPO, but also in other AOP processes like catalytic wet air oxidation (CWAO) (Arena et al. 2003; Santos et al. 2005). Cu^{2+} dissolution is often at a lower extent under neutral and alkaline conditions, while the solution acidification is inevitable because of the generation of short-chain acids during the reaction process. In addition, the dissolution decreased as the oxidation reaction temperature increases from 383 to 413 K. The reason for this trend is that acids can be oxidized quickly at higher temperatures (Zapico et al. 2017).

However, there were rare discussion on the relationship between the catalytic oxidation of organic compound and metal dissolution, especially for supported copper-based catalyst in CWPO system. More importantly, the catalytic synergetic effect between Cu and Cu^+ has been proposed and verified by Shen et al. (2023). The active Cu^+ sites may further enhance the catalytic performance. The findings in the literature reflect that the valence of active metal component can be important to their catalytic performance. In principle, different calcination atmosphere can lead to different valence of metal component on catalyst. Thus, it is necessary to investigate the influence of the calcination atmosphere of catalyst during catalyst preparation on the chemical status of Cu on catalyst, as well as its consequence for the CWPO performance accordingly.

In this paper, $\text{Cu}/\text{Al}_2\text{O}_3$ -air and $\text{Cu}/\text{Al}_2\text{O}_3$ - H_2 were prepared and used for CWPO of phenol in simulated phenol

solutions. It was found that $\text{Cu}/\text{Al}_2\text{O}_3$ - H_2 performed excellently at optimum conditions. It is interesting to find that the reaction rate was faster at higher temperatures, while the Cu^{2+} dissolution was lower. Based on the observed regulations, a catalytic reaction mechanism is proposed and the feasibility of this mechanism is discussed.

Materials and methods

Materials

Alumina (Al_2O_3 , cylinder in shape) were purchased from Nantong Jinqi Chemical Co., Ltd. copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, AR, 99 ~ 102%), hydrogen peroxide (H_2O_2 , $\geq 30\%$), phenol ($\text{C}_6\text{H}_5\text{OH}$, AR, $\geq 99.0\%$), methanol (CH_3OH , AR, $\geq 99.5\%$), isopropanol ($\text{C}_3\text{H}_8\text{O}$, AR, $\geq 99.7\%$), t-butanol ($\text{C}_4\text{H}_{10}\text{O}$, AR, $\geq 99.5\%$), ammonium chloride (NH_4Cl , AR, $\geq 99.5\%$), ammonium solution (NH_4OH , AR, (NH_3) 25 ~ 28%) were obtained from Sinopharm Group Chemical Reagent Co., Ltd. Sodium diethyldithiocarbamate trihydrate ($\text{C}_5\text{H}_{10}\text{NNaS}_2 \cdot 3\text{H}_2\text{O}$, AR 99%) were obtained from Shanghai McLean Biochemical Technology Co., Ltd. High purity hydrogen gas (99.999%) was purchased from Qingdao Henglaixiang Trading Co., Ltd. Deionized (DI) water was used to prepare all of the solutions in this work.

Catalyst preparation

The catalysts were prepared by an equal volume impregnation method. First, Al_2O_3 particles as catalytic support were milled into small particles in a mortar, and the 20–40 mesh particles were selected using sieves. Then the sieved Al_2O_3 were calcined at 500 °C for 4 h in a muffle furnace. A 3.775 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ sample was dissolved in 6.75 mL DI water. Then the solution was added to 9.0 g Al_2O_3 . Theoretical mass percentage of the Cu metal in target catalyst was 10 wt.% and the volume of solution was equal to the Al_2O_3 pore volume. After a 12 h wetness impregnation, the impregnated Al_2O_3 was put in an oven at 120 °C for 4 h for drying, and then calcined at 600 °C for 3 h in a muffle furnace. The catalyst obtained was named as $\text{Cu}/\text{Al}_2\text{O}_3$ -air. Then, $\text{Cu}/\text{Al}_2\text{O}_3$ -air was further treated by H_2 at 600 °C for 3 h, and the obtained catalyst was named as $\text{Cu}/\text{Al}_2\text{O}_3$ - H_2 .

Catalyst characterization

X-ray diffraction (XRD) patterns of the catalysts were obtained with a Malvern Panalytical Empyrean diffractometer and using nickel-filtered Cu K_α radiation. The patterns were recorded over $5^\circ < 2\theta < 75^\circ$ using a scanning rate of $0.02^\circ/\text{s}$. The Brunauer–Emmett–Teller (BET) specific surface area was measured using Micromeritics TriStar 3020

automatic adsorption analyzer. N_2 adsorption isotherms at 77 K were used for textural studied with. The samples were degassed at 300 °C for 8 h, using liquid nitrogen as the cold trap and high-purity nitrogen as the adsorbate. X-ray photoelectron spectrum (XPS) and Auger electron spectrum (AES) were obtained by an X-ray photoelectron spectroscope (Thermo SCIENTIFIC ESCALAB250Xi) with an Al $K\alpha$ radiation source.

Catalytic activity evaluation

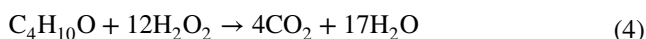
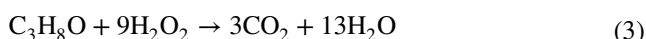
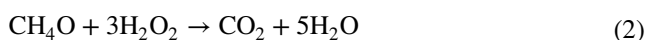
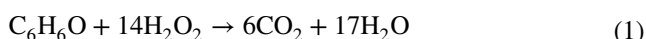
The degradation of simulate wastewater was studied using a custom reactor as shown in Fig. 1. A round-bottomed flask with water bath was used for stable temperatures. A magnetic stirrer was used to keep the stirring speed. The solution volume was 200 mL and concentration of phenol was 280 mg/L. Before catalyst was added, the substrate solution was stirred for several minutes to reach a target temperature. Samples were taken out of the solution waiting for analysis, and taken as the initial value. After catalyst was added, there was a 10 min equilibrium period before starting the catalytic tests. As soon as 2.0 mL H_2O_2 was added (14.0 mol of H_2O_2 is required to degrade 1.0 mol of phenol stoichiometrically, and 2.0 mL 30 wt.% H_2O_2 is enough to degrade 200 mL of 280 mg/L phenol), the reaction started. Typically, samples were withdrawn from the solution at regular time intervals for one of the chemical oxygen demand (COD) (1 mL sample for each time measurement), total organic carbon (TOC) (5 mL sample) and UV absorption spectroscopic (2

mL sample) analysis. Typically, a 2 mL sample was withdrawn for measuring the Cu^{2+} concentration after 60 min of reaction.

The effects of three influencing factors including calcination atmosphere during catalytic preparation, reaction temperature in the catalytic test, and free radical trapping agents on catalytic reaction rates was studied. The effect of different calcination atmosphere, reaction temperature on the metal ion dissolution amount was also examined.

Quenching experiment

Before H_2O_2 was added, three quenching agents (methanol of 160 mg/L, isopropanol of 300 mg/L, and t-butanol of 375 mg/L) were mixed with three phenol oxidation systems, respectively. The concentrations of three quenching agents were controlled to be 5.0 mmol/L. Stoichiometrically, the organics was sufficient to be oxidized completely by H_2O_2 according to Eqs. (1–4). The samples were withdrawn at different times during the reaction for determination.



Analytical methods for reaction solution

The samples were taken out from the solution during the reaction. Then the samples were diluted by DI water and analyzed through the following methods. The content of organics in water was determined by COD (HACH DR1010) and TOC (Shimadzu TOC-L CPH). The COD and TOC removal rates were calculated using Eq. (5) and Eq. (6):

$$COD\ removal\% = (1 - COD_t/COD_0) * 100\% \quad (5)$$

$$TOC\ removal\% = (1 - TOC_t/TOC_0) * 100\% \quad (6)$$

where COD_t and TOC_t were the COD and TOC values at the reaction time of t min, respectively. And COD_0 and TOC_0 were the initial value at the reaction time of 0 min, respectively.

Copper ions was colored by sodium diethyldithiocarbamate under alkaline conditions, and then determined by Ultraviolet–visible (UV–Vis) absorption spectroscopy (Analytik Jena AG) at 453 nm. The copper ion concentrations were calculated through the Eq. (7):

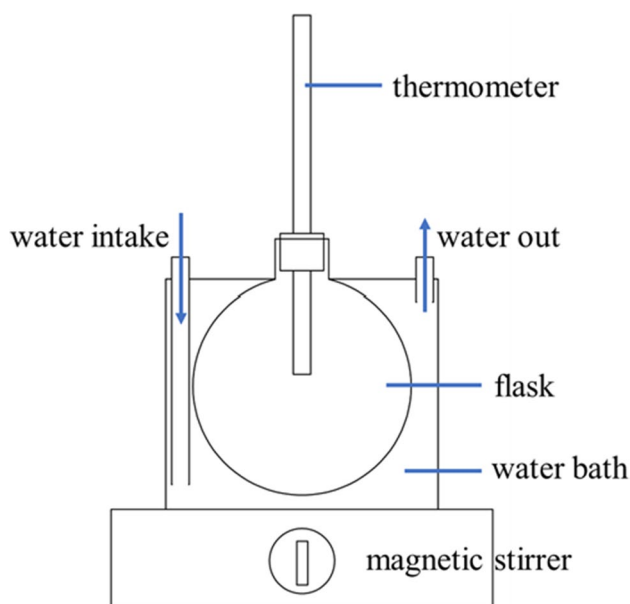


Fig. 1 Diagram of experimental setup for catalytic oxidation of phenol in water

$$\text{Metal dissolution (mg/L)} = \text{Abs} / (0.0016 * V) \quad (7)$$

where *Abs* was the absorbance of the colored solution, *V* was the volume of solution taken from the target sample solution, and 0.0016 was the slope of the standard curve for the relationship between Cu^{2+} and *Abs*. A series of Cu^{2+} solutions were prepared with different known concentration of Cu^{2+} (Cu mass basis) for the standard curve. The standard curve (with a zero intercept) was then obtained by plotting the absorbance (at 453 nm) of different Cu^{2+} solutions over their Cu^{2+} mass in a fix total volume of solution.

UV–Vis was also used to judge the changes of characteristic peaks of phenol (271 nm) and intermediates.

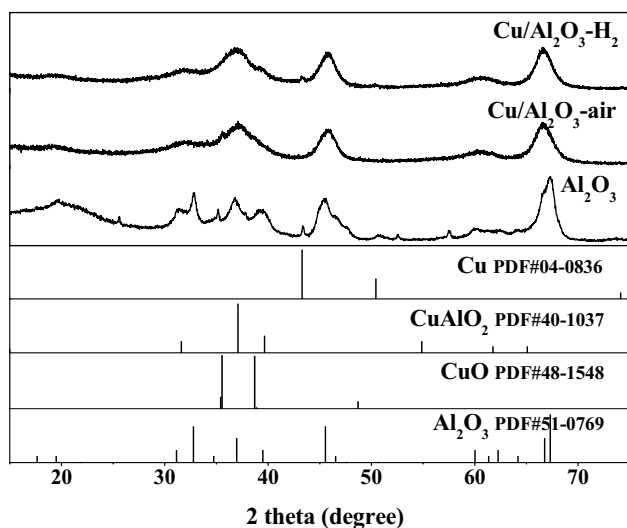
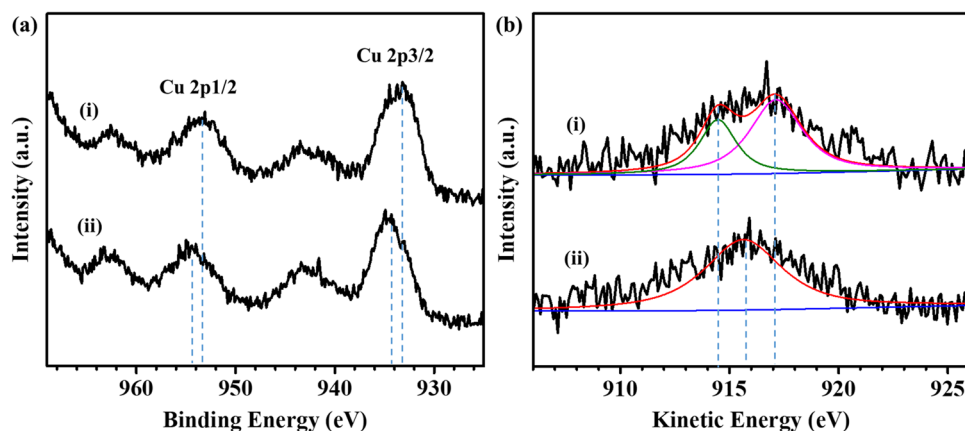


Fig. 2 XRD patterns of copper-based catalysts compared with selected standard diffraction pattern from the JCPDS card

Fig. 3 (a) High-resolution XPS spectrum of Cu 2p and (b) AES spectrum of Cu for catalysts. (i) $\text{Cu}/\text{Al}_2\text{O}_3\text{-H}_2$ and (ii) $\text{Cu}/\text{Al}_2\text{O}_3\text{-air}$



Results and discussion

Characterization of basic physiochemical properties

XRD

The XRD pattern of catalysts and catalytic support are shown in Fig. 2. The diffraction peaks of Al_2O_3 at 2θ of 33.3, 35.7, 66.8° corresponded well to (107), (114) and (1114) lattice planes of aluminum oxide- Al_2O_3 (PDF-#51–0769) (Zapico et al. 2017). The diffraction peaks of Al_2O_3 were weakened after the Cu component was loaded, while position of Al_2O_3 diffraction peaks were not changed. The Al_2O_3 peaks of $\text{Cu}/\text{Al}_2\text{O}_3\text{-air}$ and $\text{Cu}/\text{Al}_2\text{O}_3\text{-H}_2$ remained unchanged. The diffraction peaks of $\text{Cu}/\text{Al}_2\text{O}_3\text{-air}$ at 2θ of 35.4, 35.5 and 38.7°, corresponded respectively to (002), (11–1) and (111) lattice planes of tenorite-CuO (PDF-#48–1548) (Xin et al. 2021). The diffraction peaks of $\text{Cu}/\text{Al}_2\text{O}_3\text{-H}_2$ at 2θ of 43.3, 50.4 and 74.1°, corresponded to (111), (200) and (220) lattice planes of copper-Cu (PDF-#04–0836). In addition, diffraction peaks of CuAlO_2 (PDF-#40–1037) existed in both $\text{Cu}/\text{Al}_2\text{O}_3\text{-air}$ and $\text{Cu}/\text{Al}_2\text{O}_3\text{-H}_2$ samples. In contrast, to that the peaks assigning to CuO were not observed in $\text{Cu}/\text{Al}_2\text{O}_3\text{-H}_2$. This difference indicated that the interaction of Cu and Al in CuAlO_2 was stronger than Cu and O in CuO, and Cu(I) was difficult to be further reduced. Therefore, the CuAlO_2 peak was still observed after calcination under H_2 atmosphere. The results indicated that the Cu components existed as CuO and CuAlO_2 in $\text{Cu}/\text{Al}_2\text{O}_3\text{-air}$ catalyst, while existed as Cu and CuAlO_2 in $\text{Cu}/\text{Al}_2\text{O}_3\text{-H}_2$ catalyst.

XPS

The XPS was then used to further investigate the chemical status of Cu in $\text{Cu}/\text{Al}_2\text{O}_3\text{-H}_2$ and $\text{Cu}/\text{Al}_2\text{O}_3\text{-air}$ (Fig. 3). In Fig. 3a, two peaks located at around ~933 and ~953 eV and strong satellite peaks can be clearly seen from the

high-resolution Cu 2p XPS spectrum. The peak at ~ 953 eV can be assigned to Cu. Satellite peaks still existed after the H_2 calcination, which indicated the possibility of Cu(II). The two catalysts had similar peaks, but there was a slight difference. The binding energy of Cu 2p $_{1/2}$ shifted from ~ 965.5 (in Cu/ Al_2O_3 -air) to ~ 966.7 eV (in Cu/ Al_2O_3 - H_2) and Cu 2p $_{3/2}$ shifted from ~ 934.6 (in Cu/ Al_2O_3 -air) to ~ 933.3 eV (in Cu/ Al_2O_3 - H_2) (Larson 1974; Huang et al. 2019). It indicated that Cu(II) partially transformed to Cu(I) and Cu(0) after calcination in H_2 . The AES spectrum (Fig. 3b) shows the peak of ~ 915.8 eV was shift to ~ 914.5 and ~ 917.2 eV after calcined in H_2 (Shen et al. 2023). The peak of Cu/ Al_2O_3 -air was assigned to Cu (II) and two peaks of Cu/ Al_2O_3 - H_2 can be corresponded to Cu(I) and Cu(0), respectively. This indicated that the Cu(I) and Cu(0) existed in Cu/ Al_2O_3 - H_2 . Combining the results of high-resolution Cu 2p and AES spectra, the Cu component existed mainly as Cu(II) in Cu/ Al_2O_3 -air, and existed as Cu(I), Cu(0) and Cu(II) in Cu/ Al_2O_3 - H_2 . The results of XPS were consistent with the results of XRD and further indicated the existence of Cu with different valence, which is beneficial for studying the relationship between the chemical status of catalyst and its catalytic performance.

N_2 adsorption–desorption isotherm

The 77K- N_2 adsorption–desorption isotherms are shown in Fig. 4. Both of these N_2 adsorption–desorption isotherms belonged to an IUPAC type IV isotherm with a H1 hysteresis loop (Yang et al. 2021). This indicated that the catalysts were mesoporous and had uniform pore size distributions. The BET surface area, pore volume and pore width of Al_2O_3 , Cu/ Al_2O_3 -air and Cu/ Al_2O_3 - H_2 obtained from the N_2 adsorption–desorption isotherms are listed in Table 1. It can be noticed that the BET surface area and pore volume of catalyst was decreased (from 163 to 142 m^2/g for Cu/ Al_2O_3 -air for BET area for instance), while the pore width increased (from 10.7 to 13.7 nm for Cu/ Al_2O_3 -air for instance). The changes in pore volume and pore size suggested that a part

Table 1 Physicochemical properties of the Cu catalysts compared to the support

	BET surface area/ $m^2 \cdot g^{-1}$	Pore volume/ $cm^3 \cdot g^{-1}$	Pore width/nm	External area/ $m^2 \cdot g^{-1}$
Al_2O_3	163	0.62	10.73	166
Cu/ Al_2O_3 -air	142	0.60	13.73	130
Cu/ Al_2O_3 - H_2	131	0.58	13.71	120

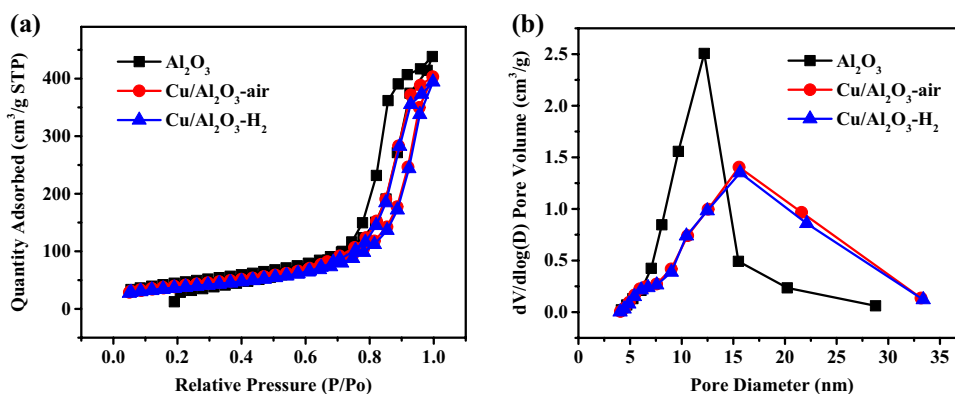
of pores were occupied by Cu component, and these occupied pores were mainly smaller pores. The BET surface area was further decreased from 142 to 131 m^2/g for Cu/ Al_2O_3 - H_2 . However, the pore width was almost unchanged (13.7 nm). This phenomenon suggested that the pores were further filled due to the clustered Cu(0), and Cu(0) was obtained from reduction of Cu(II) by H_2 in the "XRD" Section.

Influence factors for the catalytic performance in phenol oxidation by H_2O_2 in water

Reaction temperature

The performance of different catalysts was evaluated by phenol oxidation reaction with H_2O_2 . To determine the catalytic activity at an optimal reaction temperature, the COD removal rates were calculated and the UV absorption spectrums of the solution were measured during the reaction process. The COD removal rate of phenol gradually increased with the increase of reaction temperature before reaching 70 °C (Fig. 5). Unexpectedly, the initial reaction rate at 80 °C was faster than 70 °C, while the COD removal rate at 80 °C was lower at the reaction rate of 60 min. The reason can be accounted to the case that high temperature promoted the catalytic degradation reaction on one hand, and self-decomposition rate of H_2O_2 to H_2O and O_2 was also accelerated on the other (Luo et al. 2020; Xia et al. 2011; Liang et al. 2019). Therefore, the optimal reaction temperature was 70 °C, since at this condition the catalytic reaction

Fig. 4 (a) N_2 adsorption–desorption isotherms and (b) pore size distribution of the Cu catalysts



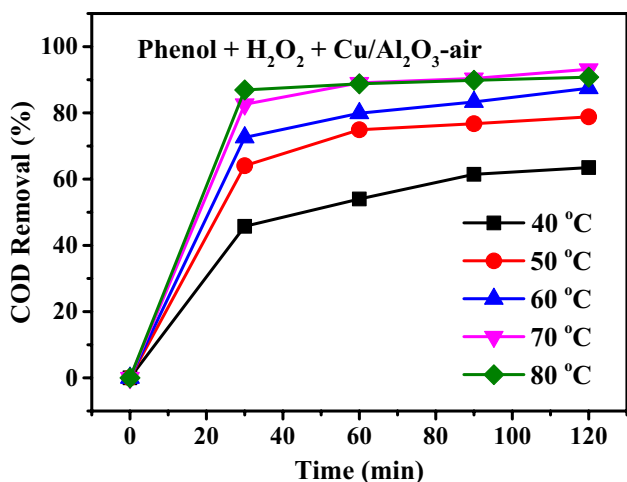


Fig. 5 Effect of reaction temperature on the catalytic reactions. Reaction conditions: concentration of phenol=280 mg/L, Cu/Al₂O₃-air dosage=5 g/L, H₂O₂ dosage=0.09 mol/L

rate and self-decomposition of H₂O₂ were comprehensively considered.

The UV absorption spectrums of solution during reaction are shown in Fig. 6a (40 °C) and 5b (70 °C). As expected, the characteristic peak of phenol at 270 nm decreased slightly at 40 °C. There was a UV absorption band in the wavelength

range of 190 and 260 nm, indicating that a large number of degradation intermediates still existed in the solution, such as hydroquinone, resorcinol, p-benzoquinone, and catechol (Huang et al. 2021a; Taran et al. 2018). The characteristic peak of phenol decreased significantly at 70 °C. However, the COD removal rate finally stabilized around 93% at 70 °C, which was due to the residual organic small molecules that were difficult to degrade, such as formic acid, acetic acid and oxalic acid (Guo et al. 2021).

Calcination atmosphere during catalyst preparation

In order to study the effect of calcination atmosphere on catalyst activity, Cu/Al₂O₃-air and Cu/Al₂O₃-H₂ were used for catalytic oxidation reactions for comparison. The COD removal rates during reactions were measured and compared. The result can be seen in Fig. 7.

Compared with the case of no catalyst being used (-None in Fig. 7a), the reaction was promoted by two catalysts effectively (Fig. 7a). The COD removal rate was nearly not observable at 40 °C when no catalyst was used. There was no visible change in color during the reaction process. In the presence of catalyst, the solution turned brown and gradually faded as the reaction proceed, which suggested that p-benzoquinone was generated and discussed in the "Reaction temperature" Section. It was

Fig. 6 The ultraviolet absorption spectrum of solution during reaction at (a) 40 °C and (b) 70 °C. Reaction conditions: concentration of phenol=280 mg/L, Cu/Al₂O₃-air dosage=5 g/L, H₂O₂ dosage=0.09 mol/L

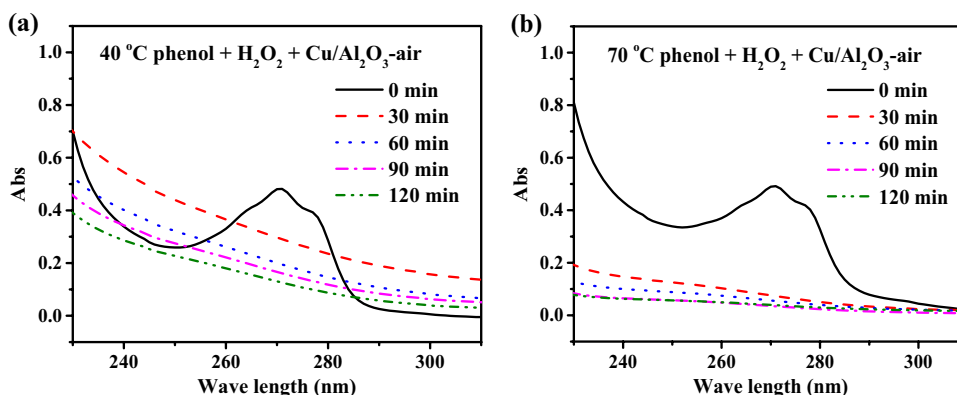
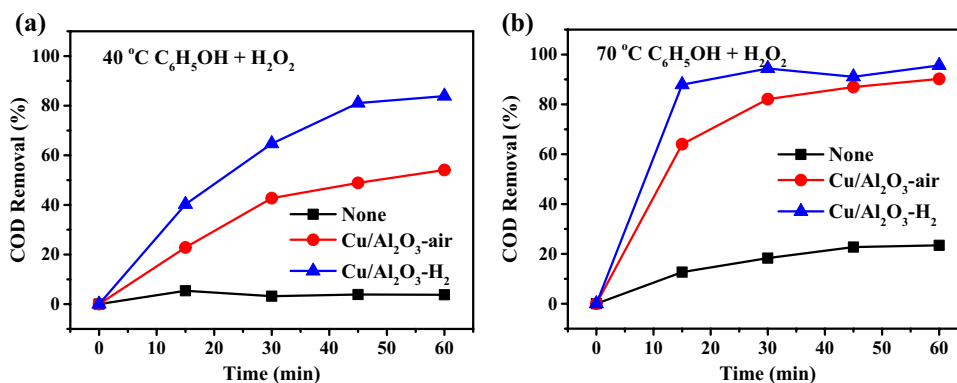


Fig. 7 Catalytic performance of Cu/Al₂O₃-air and Cu/Al₂O₃-H₂ at different temperatures of (a) 40 °C and (b) 70 °C. Reaction conditions: concentration of phenol=280 mg/L, catalysts dosage=5 g/L, H₂O₂ dosage=0.09 mol/L



difficult to oxidize phenol at 40 °C. The COD removal rate of Cu/Al₂O₃-H₂ (~82%) at 1 h was significantly higher than that of Cu/Al₂O₃-air catalyst (~52%) at 1 h.

In Fig. 7b, it can be seen that the COD removal rate (~22%) was higher than 40 °C at 70 °C after 1 h reaction even without using catalyst. This may be due to self-decomposition of H₂O₂ at 70 °C, generating reactive oxidant species. At 70 °C, Al₂O₃ replaced the catalyst as comparison, and the catalytic test results for the pure support were presented in Supporting Information (Figure S1). The results show that there was no significant change in COD removal compared to the case without using catalyst after reaction. The COD removal rate was significantly improved and the color of the reaction solution changed rapidly after a certain catalyst was added. As expected, the catalytic performance of Cu/Al₂O₃-H₂ was better than Cu/Al₂O₃-air in terms of COD removal rate. In principle, the COD removal may also be contributed from the adsorption of organic compounds by the catalyst during the catalytic reaction. Therefore, the adsorption experiment of Al₂O₃, Cu/Al₂O₃-air and Cu/Al₂O₃-H₂ without hydrogen peroxide was performed to investigate the adsorption effect (in Figure S2). It was found that the adsorption effect of the catalysts was not significant in the reaction from Figure S2.

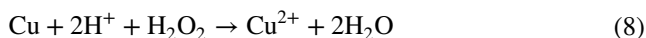
The Cu component in Cu/Al₂O₃-air were existed in form of high valent oxides, which was an inactive state for CWPO. After calcined by H₂, high valent Cu oxides were converted into zero or low valent oxides (Cu(I)) (see "XRD" and "XPS" Section). For example, Cu elements in CuAlO₂ and Cu were existed in the form of Cu(0) and Cu(I) according to the XRD results. These states were conducive to the redox reactions, and could have an excellent catalytic activity accordingly. H₂O₂ would react with Cu(0) and Cu(I) to generate ·OH, and react with Cu(I) and Cu(II) to generate ·OH (Huang et al. 2021b). Therefore, the catalytic performance of Cu/Al₂O₃-H₂ was better than Cu/Al₂O₃-air under the same conditions. However, the COD removal rate did not reach to 100%, which was due to the formation of some refractory small organic molecules. These molecules existed at a low concentration that were difficult to degrade.

Reusability is important for a catalyst. The reusability performance of the two Cu catalysts was tested through five consecutive experiments. The results are shown in Figure S3. From the results shown in Figure S3, Cu/Al₂O₃-H₂ showed an excellent catalytic performance after 4 cycles of recycling without a significant decrease in COD removal rate. Compared to Cu/Al₂O₃-air, the recyclability performance of Cu/Al₂O₃-H₂ was better. One possible reason was that the interaction between the active metal and the carrier was stronger after calcination in H₂, resulting in less Cu²⁺ dissolution amounts (vide infra).

Effects of reaction temperature and calcination atmosphere on metal dissolution

In order to investigate the factors affecting the Cu²⁺ dissolution amount in solution, the metal dissolution amounts (in terms of Cu²⁺ concentration) of catalysts in DI water, H₂O₂ aqueous solution, phenol aqueous solution, and the solution after catalytic oxidation were measured at different temperatures (Fig. 8). The dissolution amounts were under 5 mg/L in DI water, H₂O₂ aqueous solution and phenol aqueous solution. There are some differences in copper dissolution due to wear caused by stirring. In other words, DI water, H₂O₂ and phenol had a weak effect on promoting the Cu²⁺ dissolution in the Cu/Al₂O₃-air system.

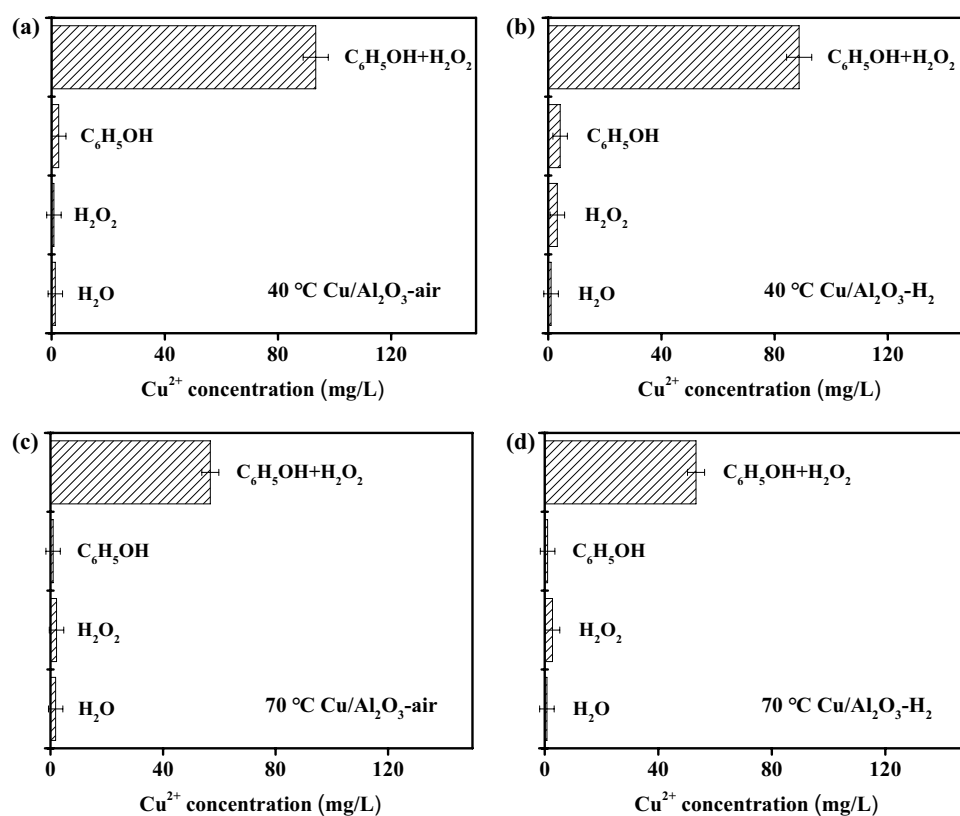
An obvious ions dissolution was observed for the catalytic oxidation reaction system, partly because the process of oxidation and reduction of the Cu component was involved in the reaction solution. Interestingly, the Cu²⁺ amount decreased significantly as the reaction temperature increased from 40 °C to 70 °C. There are two competitive reactions of H₂O₂ during the phenol oxidation (Eqs. (1) and (8)).



The oxidation rate of phenol was slow at 40 °C (Eq. (1)). In addition, H⁺ may be ionized from small molecular acids generated during the oxidation process (Guo et al. 2021). And excessive H₂O₂ remained in the solution, where Eq. (8) was promoted. While Eq. (1) was faster at 70 °C, H₂O₂ was utilized effectively to convert into ·OH (discussed in the "Quenching experiments of reactive oxidant species" Section) and reacted with organic compounds. The competitive Eq. (8) decelerated due to fewer reactants. Correspondingly, the Cu²⁺ dissolution amount was decreased. Compared with Cu/Al₂O₃-air, Cu/Al₂O₃-H₂ has a slightly reduced Cu²⁺ dissolution amount, and at the same time had a better catalytic performance (in the "Calcination atmosphere during catalyst preparation" Section). The Cu component existed as Cu(0) and Cu(I) in Cu/Al₂O₃-H₂. It reflected that the interaction between metal and carrier in Cu/Al₂O₃-H₂ was stronger, leading to a lower metal dissolution than Cu/Al₂O₃-air.

Based on the results mentioned above, DI water, H₂O₂ and phenol alone could not promote ion dissolution. Pretreatment with H₂ could improve the catalytic performance and reduce the dissolution of metal ions slightly. Meanwhile, it was also found that the catalytic reaction rate was accelerated and metal dissolution was reduced at a higher temperature. This phenomenon is undoubtedly beneficial to reducing metal ion pollution and saving post-treatment costs.

Fig. 8 Metal dissolution of catalysts in DI water, H_2O_2 aqueous solution, phenol aqueous solution and reaction solution at different temperature: (a) 40 °C Cu/ Al_2O_3 -air, (b) 40 °C Cu/ Al_2O_3 - H_2 , (c) 70 °C Cu/ Al_2O_3 -air and (d) 70 °C Cu/ Al_2O_3 - H_2 . Reaction conditions: concentration of phenol = 280 mg/L, catalysts dosage = 5 g/L, H_2O_2 dosage = 0.09 mol/L



Quenching experiments of reactive oxidant species

Alcohols are usually applied as hydroxyl radical scavengers, such as methanol, isopropanol and t-butanol (Schneider et al. 2020; Huang et al. 2021b; Yang et al. 2021; Manos et al. 2022). Quenching experiments were performed to confirm that the catalytic oxidation of phenol by H_2O_2 over copper based catalysts involved a free radical oxidation mechanism. Furthermore, the reaction mechanism in the "Proposed reaction mechanism" Section was proposed based on the free radical oxidation mechanism. The UV–Vis absorption spectrums during the CWPO reactions with alcohols are obtained in Fig. 9.

The UV–Vis absorption spectrum confirmed that the absorption peaks (at 270 nm) declined evidently after methanol, isopropanol or t-butanol was added (Fig. 9a–d). These indicated that the reaction was inhibited to some extent. Since hydroxyl radical partially reacted with scavengers, and their reaction with phenol was slower in rate.

The inhibitory effect of methanol and t-butanol was similar. The position of the 10 min curve (Fig. 9d) was similar to the position of the 30 min ~ 60 min curve (Fig. 9a and c). Isopropanol had the optimum inhibitory effect. The substances with higher electron density tend to be preferentially attacked by free radicals (Lin et al. 2023). The electronegativity of O^{2-} in an organic compound follows the order of t-butanol > isopropanol > methanol. Unexpectedly,

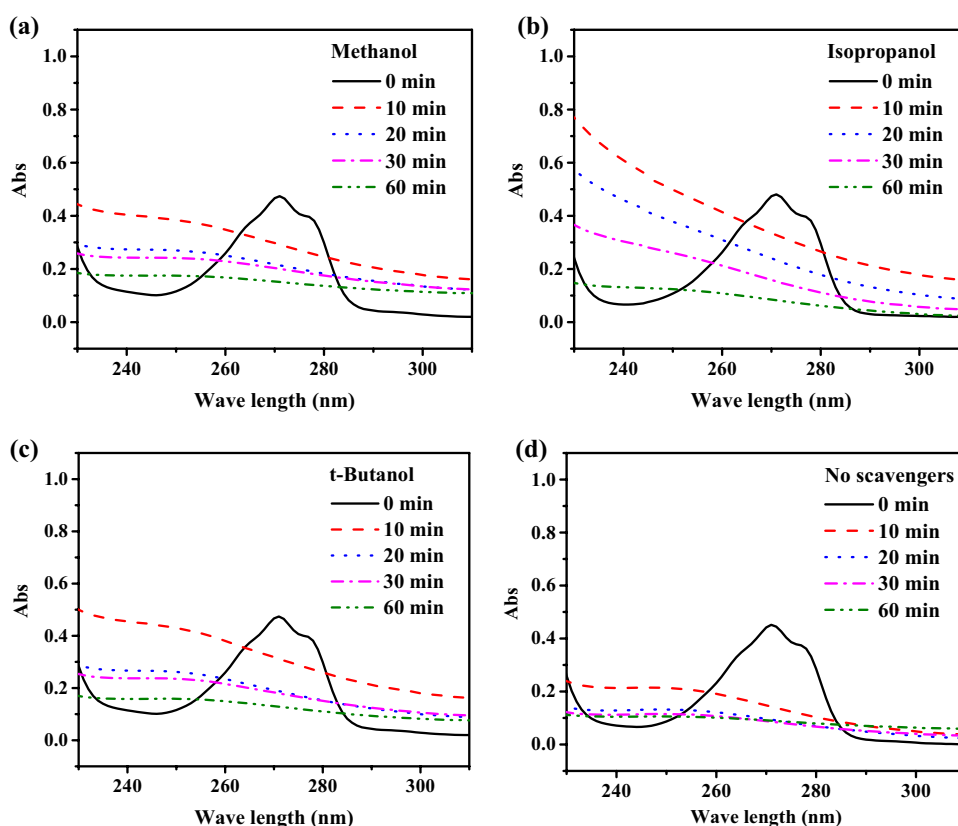
isopropanol had a better inhibitory effect eventually. This might be due to its smaller steric hindrance. The inhibitory effect of t-butanol was similar to that of methanol due to steric hindrance.

When the reaction was inhibited, the CWPO solution was observed to be brown. It was just similar to the case of the reaction occurred at 40 °C (see "Calcination atmosphere during catalyst preparation" Section). A new absorption peak appeared (~246 nm), indicating the formation of p-benzoquinone or its analogues during phenol degradation (Kuboyama et al. 1974). This peak decreased slowly as the reaction continued. In addition, isopropanol had the optimum inhibitory effect which made the transition process occurred more slowly. The results indicated that the production of hydroxyl radical was promoted by catalysts during the reaction. This process can be inhibited after adding radical scavengers.

Proposed reaction mechanism

In above sections, the effects of reaction temperature and calcination atmosphere in the catalyst preparation process on catalytic reaction rates and dissolution of the Cu component were studied in the "Influence factors for the catalytic performance in phenol oxidation by H_2O_2 in water" and "Effects of reaction temperature and calcination atmosphere on metal dissolution" Sections, and the free radical quenching experiments were performed in the

Fig. 9 UV–Vis absorption spectrum during the CWPO reactions at the presence of hydroxyl radical scavengers: (a) Methanol; (b) Isopropanol; (c) t-Butanol; (d) no scavengers as comparison. Reaction conditions: concentration of phenol = 280 mg/L, Cu/Al₂O₃-H₂ dosage = 5 g/L, H₂O₂ dosage = 0.09 mol/L



"Quenching experiments of reactive oxidant species" Section. Some interesting clues can be seen in the catalytic reaction results. Especially, the Cu dissolution amount in the reaction was much more than the non-reaction system, and when the reaction temperature was higher, the dissolution amount was lower. To better explain the process of catalytic reaction of Cu-catalyzed phenol oxidation as well as the Cu²⁺ dissolution behavior, the catalytic mechanism of Cu/Al₂O₃-H₂ was further proposed, discussed and tested. The proposed reaction mechanism is summarized in Fig. 10.

The reactants in the proposed catalytic reaction mechanism involves the Cu component, phenol, and H₂O₂, as shown in Fig. 10. At first, the possible reactions between the Cu component and H₂O₂ and their consequences were discussed. The reaction began as soon as H₂O₂ was added into the reaction system. H₂O₂ can be converted into ·OH and ·OOH, respectively catalyzed by Cu(0) and Cu(I) (Huang et al. 2021b; Covinich et al. 2016), and the Cu component on the catalyst completed valence conversion in this process. The ·OOH might contribute to the overall catalytic oxidation reactions which had not been confirmed, and was considered as product of the valence transition of the catalyst in this work. Therefore, in the proposed mechanism in Fig. 10, four possible reactions (Eqs. (9–12)) are included.

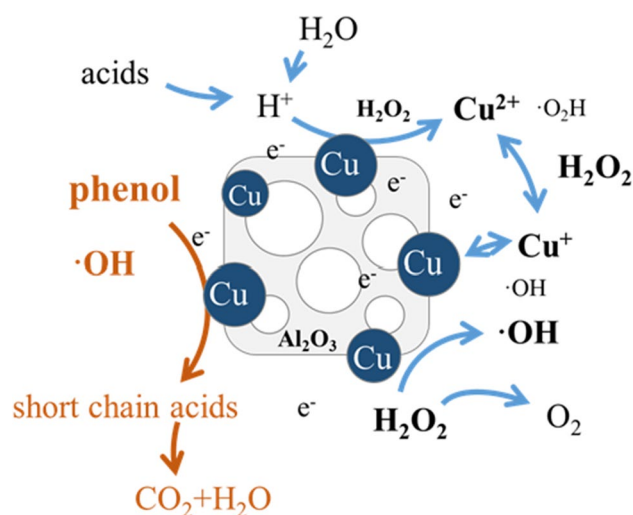


Fig. 10 Proposed reaction mechanism of phenol oxidation by H₂O₂ catalyzed by Cu/Al₂O₃-H₂

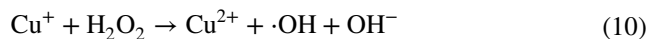
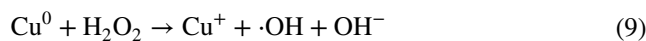
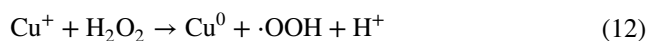
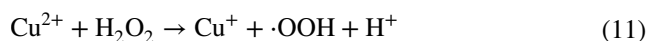


Table 2 The changes of Cu²⁺ dissolution, pH and TOC removal % during the reaction. Reaction conditions: concentration of phenol = 280 mg/L, Cu/Al₂O₃-H₂ dosage = 5 g/L, H₂O₂ dosage = 0.09 mol/L

	Phenol solution	Reaction time (min)				
		0 (H ₂ O ₂ added)	10	20	30	60
Cu ²⁺ dissolution (mg/L)	2.93	4.72	63.4	67.8	61.1	67.4
pH	6.68	8.19	5.99	6.21	6.27	6.22
TOC removal %	-	0	88.3	92.5	94.3	96.8



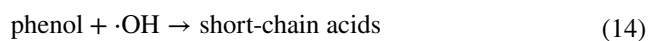
In the above reactions, Cu(0) and Cu(I) reacted with H₂O₂ to generate Cu(II). This process can occur in the solution or on the surface of the catalyst. However, when catalysts and H₂O₂ existed alone in the solution at 40 °C and 70 °C (see in Fig. 8), there was no significant Cu²⁺ dissolution. This phenomenon implicated that the Cu(II) species generated in this process existed on the surface of the catalyst rather than in the aqueous solution when the solution was non-acidic. However, situations may be different if the solution is acidic, that is, H₂O₂ could lead to a side reaction of Cu²⁺ dissolution under acidic conditions (Eq. 8), and this reaction was a competitive reaction of Eq. 1 (discussed in the "Effects of reaction temperature and calcination atmosphere on metal dissolution" Section).

Secondly, when the solution system only contained catalysts and phenol, there was rather lower Cu²⁺ dissolution amount (see in Fig. 8). This is due to the absence of H₂O₂, and thus no more Cu²⁺ can be generated through the reactions (Eqs. 9–10).

Thirdly, based on the above two points of discussion, the Cu²⁺ dissolution behavior is explainable when both of phenol and H₂O₂ existed in the CWPO reaction system. The ·OH reacted with phenol to generate CO₂ and H₂O (Eq. 13). The existences of ·OH species was supported by the quenching experiments in the "Quenching experiments of reactive oxidant species" Section, indicating the contribution of ·OH to the catalytic reaction.



However, the above process was not completed only in one step. The phenol was oxidized to converted into short-chain acids firstly (Eq. 14) (Guo et al. 2021; Taran et al. 2018). Then, short-chain acids were further oxidized to CO₂ and H₂O eventually (Eq. 15).



When the reaction temperature was higher, the COD removal was higher (Figs. 5 and 7) and the Cu²⁺ dissolution

was lower (Fig. 8). This trend was explainable with the aid of Eqs. (13–15) as follows. When phenol in water was more completely mineralized (Eq. 13), the contribution of Eq. 14 and Eq. 15 was less. Thus, the concentration of the short-chain acids including their electroionized forms was less. Since the short-chain acids were important species for maintaining the system acidity during the CWPO reaction, and the acidic conditions were the main reason for the Cu²⁺ dissolution, therefore, the Cu²⁺ dissolution amount was lower when phenol was more completed degraded.

In addition, part of H₂O₂ may not completely converted into ·OH, accompanied with self-decomposition (Eq. 16). This process can be accelerated at high temperatures. The reactive oxidant species, like ·OH and ·OOH, may not completely interact with organic matters, and may also be consumed by themselves (Eq. 17).



To better support the reaction mechanism proposed above as well as in Fig. 10, the TOC removal rates, Cu²⁺ dissolution and pH values during the reaction are collected in Table 2. Due to the dissociation of H⁺ by water and the weak acidity of the phenol solution (pH = 6.68), a small amount of Cu²⁺ was dissolved in the solution. After the catalyst reached adsorption saturation, the solution become alkaline slightly. As soon as the reaction began, short-chain acids were formed from phenol, which can produce H⁺ by ionization, and then oxidized to CO₂ and H₂O. During this process, the pH value decreased firstly and then increased slightly. Due to the dissolution of CO₂ and refractory short-chain acids solution with a low concentration, the final pH value of the solution was remained weakly acidic. During the reaction process, the participation of Cu component in the redox reaction and the acidic solution due to the dissociation of H⁺, leading to large metal dissolution amount.

Conclusion

In this work, the Cu/Al₂O₃-air and Cu/Al₂O₃-H₂ catalysts were prepared for the CWPO reaction of phenol. The catalytic performance and metal dissolution behavior of these

catalysts were investigated. The primary findings are summarized as follows.

- (i) The Cu/Al₂O₃-H₂ showed an excellent catalytic performance for phenol degradation under optimized reaction conditions. The COD and TOC removal rates reached to 89% and 96%, respectively. At the same time, Cu/Al₂O₃-H₂ maintained a lower Cu²⁺ dissolution amount during reaction compared to the Cu/Al₂O₃-air case.
- (ii) More interestingly, the faster the reaction rate was, the less Cu²⁺ dissolution was observed. In particular, the catalytic reaction rate at 70 °C was higher than 40 °C, and at the same time the Cu²⁺ leaching amount was lower.
- (iii) Combined with the quenching experiments, a catalytic reaction mechanism was proposed mainly for explanation of the relationship between CWPO reaction rate and dissolution amount of Cu²⁺. The proposed mechanism is consistent with experimental findings.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11356-024-32781-5>.

Author contributions Wumin Zhang: catalyst preparation, characterization, reaction test, writing. Huimin Zhuang: catalytic test, reaction setup construction, discussion. Yu Guo: catalyst preparation, characterization, paper revision. Hua Chi: catalyst preparation, characterization, reaction test. Qiuyue Ding: reaction setup construction. Lu Wang: catalyst preparation, reaction test. Yanyan Xi: catalyst characterization, discussion. Xufeng Lin: idea development, research funding provision, writing and organization.

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Data availability The raw data presented in this study are available from the first author if request.

Declarations

Ethics approval and consent to participate Not applicable.

Consent to publish Not applicable.

Competing interests There are no conflicts to declare.

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