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The degradation of maleic acid with wet peroxide oxidation catalyzed by Al_2O_3-supported Cu catalyst: effect of inorganic ions

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Abstract

The alumina particle supported Cu component catalyst, Cu/Al_2O_3, was prepared by equal volume wet impregnation and evaluated through degradation of maleic acid with catalytic wet peroxide oxidation (CWPO) in this work. It was found that the Cu/Al_2O_3 catalyst had an excellent CWPO performance. A total organic carbon (TOC) removal rate of 98% was reached under the optimized catalytic reaction conditions. Moreover, the effect of inorganic ions on CWPO was comprehensively evaluated using different acid and alkali. The alkali had an optimum effect on TOC removal rates, while acid had an inhibitory effect. A catalytic oxidation mechanism was proposed to illustrate the CWPO process of Cu/Al_2O_3 catalyst. The catalytic test results as well as the proposed mechanism can provide an insight into the influence mechanism of inorganic ions on CWPO.

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

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Introduction

The efficient treatment of organic wastewater has developed to be an important task in environmental research. The main reason is the rapid development of modern industry, which has led to serious water shortage and pollution, affecting the survival and development for humankind 1 [1].

Several methods have been developed so far for organic pollutants treatment, such as advanced oxidation processes (AOPs). In AOPs, highly reactive oxidant species (such as ·OH) can be produced to degrade organic pollutants by decomposing oxidants (such as H_2O_2, O_3 and O_2). Wet peroxide oxidation (WPO) has drawn great attention due to its mild conditions and non-toxic, where H_2O_2 is the oxidant. The degradation rate can be accelerated by using catalysts in this process, known as catalytic wet peroxide oxidation (CWPO). Heterogeneous CWPO take the advantage of easier catalyst recycling and broader range of applications, compared to homogeneous CWPO. Nguyen et al. investigated Fe–Cu composite/H_2O_2 system for the degradation of hazardous organics [2]. Saleh and Taufik demonstrated Fe_3O_4/ZnO/graphene composites was prepared to catalytic oxidation dyes [3]. Supported metal catalysts, as a kind of heterogeneous catalyst, exhibit better catalytic performance due to its high-activity metals and carriers which provide a huge specific surface area. Wang et al. prepared an efficient Fenton system where α-Fe_2O_3/g-C_3N_4 was used as heterogeneous catalyst for pollutant degradation [4]. Lyu et al. reported mesoporous Cu/γ-Al_2O_3 was prepared by an evaporation-induced self-assembly process for the degradation and mineralization of aromatic pollutants [5]. Gosu et al. demonstrated the synthesized catalyst (copper-loaded activated alumina, Cu/AA) has phenomenal advantages in the simple separation and high removal efficiency in CWPO of catechol [6]. Hachemaoui et al. reported different metals (Cu, Cr, Fe and Zn) was loaded on mesoporous MCM-41 for CWPO of Acetaminophen [7].

Aromatic compounds are the most important pollutant in industrial wastewater. The aromatic rings will be cleaved by oxidants, resulting in the formation of short-chain carboxylic acids [8]. The residual short-chain carboxylic acids in the solution will leads to total organic carbon (TOC) value still remains unchanged after a long reaction time. These acids are often found in degradation progress of contaminants, while they are not attracted great attention due to its biodegradable and less toxic. Maleic acid (MA) is considered to be the main intermediate produced during the AOPs of aromatic compounds. Therefore, the degradation mechanism of MA may be helpful to explain the degradation process of aromatic compounds [9].

Inorganic ions have a significant impact on the performance of AOPs which is similar to other experimental factors, such as reaction temperature [10]. Choi et al. investigated the effects of anions on isopropylalcohol degradation using Fe/Al catalysts [11]. Liu et al. investigated the effect of Cl^-, NO_3^-, and PO_4^{3-} on sulfamethoxazole removal efficiency [12]. Kili et al. reported the presence of Cl^-, $SO_4^{2-}$and NO_3^- could directly interact with the organic substrate to improve its degradation rate, or led to a strong decrease in removal rate due to their lower oxidative compared to ·OH [13]. However, most of the current studies are investigated the effect of anions on the reaction rate [13, 14]. The effects of different inorganic cations existed in aqueous solutions on the degradation of organic pollutants also need to be investigated. Liu et al. investigated the effect of cations (Mg^{2+}, Cu^{2+}) on the oxidative degradation of Amoxicillin (AMX) catalyzed by nanoscale zero-valent iron (nZVI) [15]. The findings in the literatures reflect that the ions play a vital role in catalytic performance. In most cases, inorganic ions affect the reaction rates. In addition, the effect of inorganic ions on the catalytic activity should be considered. Therefore, it is necessary to investigate the influence of the different cations and anions on performance and composition of catalysts, as well as its consequence for the CWPO performance, accordingly.

In this paper, alumina particle supported Cu component catalyst, denoted as Cu/Al_2O_3, was prepared and used for CWPO of maleic acid in simulated maleic acid solutions. It was found that the Cu/Al_2O_3 catalyst with a Cu loading of 5 wt% performed excellently at optimum conditions and its Cu^{2+} dissolution was lower. It is interesting to find that the cations could lead to a higher TOC removal rates, while anions had an inhibitory effect. 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 ($Cu(NO_3)_2 \cdot 3H_2O$, AR, 99–102%), hydrogen peroxide (H_2O_2, ≥ 30%), maleic acid ($C_4H_4O_4$, CP, 99–101%), phosphoric acid (H_3PO_4, AR, ≥ 85%), nitric acid (HNO_3, AR, 35–68%), hydrochloric acid (HCl, AR, 36–38%), potassium hydroxide (KOH, AR, ≥ 85%), ammonium chloride (NH_4Cl, AR, ≥ 99.5%), ammonium solution (NH_4OH, AR, (NH_3) 25–28%) were obtained from Sinopharm Group Chemical Reagent Co., Ltd. Sodium hydroxide (NaOH, AR, ≥ 96%) were obtained from Xilong Scientific Co., Ltd. Sodium diethyldithiocarbamate trihydrate ($C_5H_{10}NNaS_2 \cdot 3H_2O$, AR 99%) were obtained from Shanghai McLean Biochemical Technology Co., Ltd. Deionized (DI) water was used to prepare all of the solutions in this work.

Catalyst preparation

The alumina particle supported Cu component catalyst, Cu/Al_2O_3, was prepared by equal volume wet impregnation. First, commercial Al_2O_3 (long cylinder strips in shape) was crushing and sieving to particles of 20–40 mesh as support. The 1.89 g $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in about 7.0 mL DI water as a precursor for impregnation. Subsequently, the Cu(II) aqueous solution was added to the 9.5 g Al_2O_3 particles drop by drop to ensure the solution evenly distributed. Then the obtain blue solid was remained overnight and dried at 393 K for 4 h. At last, calcined at 873 K for 3 h to remove nitrate and bound water. The 5 wt% Cu/Al_2O_3 (5 wt% = m $_{Cu}$: m $_{Cu/Al2O3}$) catalysts were prepared and marked as 5% Cu/Al_2O_3 catalysts. According to the above steps, 1%, 2% and 10% Cu/Al_2O_3 catalysts was prepared by changing the dissolved $Cu(NO_3)_2 \cdot 3H_2O$ content.

Catalytic activity evaluation

Maleic acid was used to evaluate the catalytic performance of Cu/Al_2O_3. The degradation reactions were performed in a 250 mL custom glass reactor with a water bath. The experimental steps were as follows. The 1 g Cu/Al_2O_3 catalyst was added to 200 mL maleic acid solution (500 mg/L). The mixture was stirred by magnetic stirrer the during all reactions. When the temperature was reached to the set value, the 30% H_2O_2 was added to the solution and the reaction was started. The aliquots were withdrawn at the regular time intervals as samples for more analysis. The used catalyst was recycled after washed by deionized water to evaluate the stability of the catalysts. The stability evaluation was the same as above typically proceeds. The influence of different ions on the reaction evaluation was similar to above typically proceeds. The difference was that 1 g Cu/Al_2O_3 catalyst was added to a 200 mL mixed solution of maleic acid (500 mg/L) and acid or alkali (concentration of phosphoric acid, nitric acid, hydrochloric acid, potassium hydroxide or sodium hydroxide was 0.0025 mol/L). The other steps were consistent with those typically proceeds described above.

Analytical methods for reaction solution

The TOC-L CPH (Shimadzu Production Institute, Kyoto, Japan) was used to analyze the total organic carbon (TOC) value. The TOC removal rate were calculated using Eq. 1:

$$\text{TOC removal}\,\% = \left(1 - \text{TOC}_t \big/ \text{TOC}_0\right) * 100\% \tag{1}$$

Here TOC_t were the TOC values at the reaction time of t min. And TOC_0 were the initial value at the reaction time of 0 min.

The determination of Cu(II) concentration was achieved by forming a yellow complex between sodium diethyldithiocarbamate and copper ions under alkaline conditions. The Ultraviolet–visible (UV–Vis) absorption spectroscopy (Analytik Jena AG) was used to measure the absorbance at 453 nm. The Cu(II) concentration was calculated through the Eq. 2:

$$\text{Metal dissolution}\,(\text{mg/L}) = Abs/(0.0016 * V) \tag{2}$$

Here 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.

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 $5° < 2\theta < 75°$ using a scanning rate of 0.02°/s.

Results and discussion

Optimization of catalytic reaction conditions

To optimize the maleic acid degradation reaction conditions, the reactions with different supported amount of Cu component, reaction temperatures and H_2O_2 concentrations were performed.

To optimize the maleic acid degradation reaction conditions, the reactions were performed with different Cu component supported amounts, reaction temperatures and H_2O_2 initial concentrations. The reaction temperature was from 303 to 343 K. When the temperature was higher than 343 K, the H_2O_2 will efficiently decomposed to O_2 and H_2O [16–18]. The H_2O_2 dosage was 0.09 mol/L tentatively in this section. Stoichometrically, the maleic acid (500 mg/L) was sufficient to be oxidized completely by H_2O_2 (0.09 mol/L).

In Fig. 1a, the TOC removal rate of maleic acid increased with the increase of Cu component supported amounts and reaction temperature. At a lower temperature (Fig. 1a), the TOC removal rate changed slowly with different Cu component supported amounts. When the temperature was higher than 323 K, the TOC removal rate increased significantly with the increased Cu component supported amounts. At 343 K, the TOC removal rate of 5% Cu/Al_2O_3 catalyst reached to 96% at 30 min.

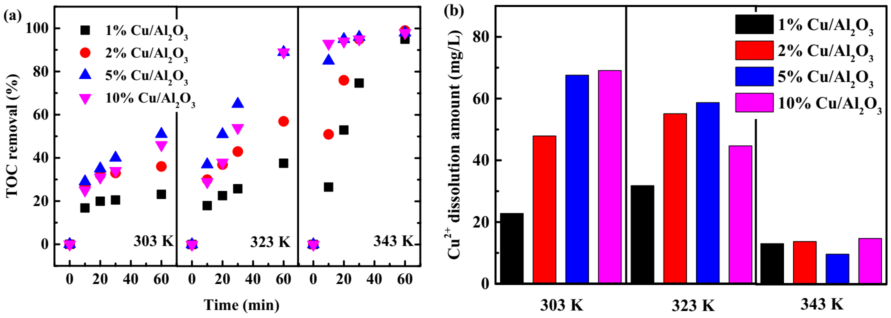

Fig. 1 Effect of the amount of Cu component on the Al_2O_3 supported catalyst and reaction temperature on **a** TOC removal rate for the maleic acid degradation and **b** Cu^{2+} dissolution amount in aqueous solution. Reaction conditions: concentration of maleic acid = 500 mg/L, catalyst dosage = 5 g/L, H_2O_2 dosage = 0.09 mol/L

It shows that the reaction temperature was more effective in improving the catalytic efficiency than the Cu component supported amounts of catalysts. Similar conclusion had also been confirmed by Qin et al. [19].

It is worth noting that the 5% Cu/Al_2O_3 catalyst with less supported Cu components also had an excellent catalytic performance which was similar to 10% Cu/Al_2O_3 catalyst. It indicated the formation of extra-framework copper species in the catalyst [20]. Correspondingly, these extra-framework copper species will finally prevent the reaction between catalytic active sites and reactants, such as H_2O_2 and maleic acid.

Accordingly, the Cu^{2+} dissolution amount of the solution after catalytic oxidation reaction was measured. In Fig. 1b, significant Cu^{2+} dissolution amount was observed in the catalytic oxidation reaction system. The reason was the involvement of the oxidation and reduction processes of Cu components during the reaction process. Interestingly, the Cu^{2+} dissolution amount decreased significantly as the reaction temperature increased from 303 to 343 K. The possible reasons are as follows.

The oxidation rate of maleic acid was slow at 303 K (Eq. 4). In addition, H^+ may be ionized from small molecular acids which generated during the oxidation process [16]. And excessive H_2O_2 remained in the solution, where Eq. 5 was promoted. At 343 K, H_2O_2 was effectively converted into ·OH catalyzed by Cu/Al_2O_3 (Eq. 3) and reacted with organic compounds (Eq. 4). The competitive Eq. 5 was decelerated due to fewer reactants. Subsequently, the Cu^{2+} dissolution amount was decreased. The 5% Cu/Al_2O_3 catalyst had an excellent catalytic performance similar to 10% Cu/Al_2O_3 catalyst. The former one also has a lower Cu component supported amounts and Cu^{2+} dissolution amounts during the reaction process.

$$H_2O_2 \rightarrow \cdot OH \tag{3}$$

$$C_4H_4O_4 + \cdot OH \rightarrow CO_2 + H_2O \tag{4}$$

$$Cu^+ + H^+ + H_2O_2 \rightarrow Cu^{2+} + H_2O \tag{5}$$

In conclusion, the TOC removal rate was proved to be strongly dependent on reaction temperature. The 5% Cu/Al_2O_3 catalyst had an excellent catalytic performance with a lower Cu component supported amounts and Cu^{2+} dissolution amounts. The TOC removal rate increased and Cu component supported amounts reduced as the reaction temperature increased. Therefore, the Cu component supported amounts and reaction temperature was confirmed as 5% and 343 K.

In order to determine the optimum concentration of H_2O_2 required in the reaction, the reaction with different initial H_2O_2 concentrations were carried out. The result was shown in Fig. 2a. The TOC removal rate increased as the concentration of H_2O_2 increased. The TOC removal rate of the reactions with 0.09, 0.13 and 0.18 mol/L H_2O_2 was much higher than that of 0.04 mol/L H_2O_2. The TOC removal rate of 0.09 mol/L and 0.13 mol/L H_2O_2 was significantly different at beginning of the reaction (0–20 min). After 20 min, the TOC removal rate was similar. The results show that the amount of ·OH produced by 0.09 mol/L H_2O_2 was sufficient to degrade 500 mg/L of maleic acid.

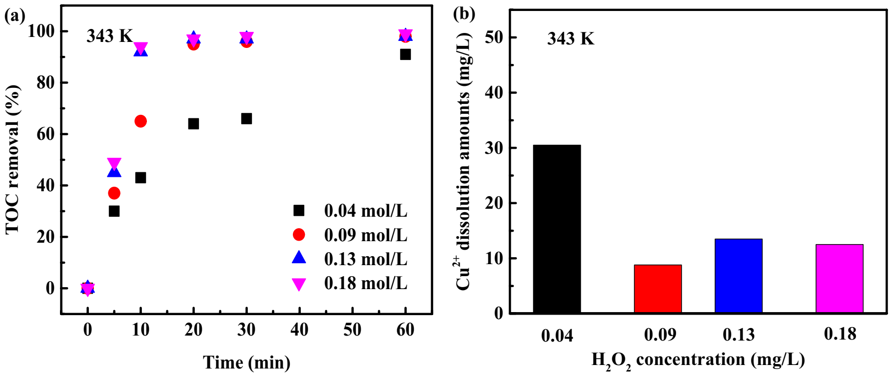

Fig. 2 The effect of H_2O_2 concentrations on **a** TOC removal rate and **b** Cu^{2+} dissolution amounts in the catalytic wet peroxide oxidation of maleic acid. Reaction conditions: concentration of maleic acid = 500 mg/L, catalyst (5% Cu/Al_2O_3) dosage = 5 g/L, reaction temperature = 343 K

When concentration of H_2O_2 was higher than 0.13 mol/L, the TOC removal rate remains unchanged due to the well-known ·OH scavenging effect (Eqs. 6–8) [11, 21].

$$H_2O_2 + \cdot OH \rightarrow H_2O + \cdot OOH \tag{6}$$

$$\cdot OH + \cdot OH \rightarrow H_2O + O \tag{7}$$

$$\cdot OH + \cdot OOH \rightarrow O_2 + H_2O \tag{8}$$

These reactions are not conducive to the reaction of organic molecules with ·OH, resulting in a proximate TOC removal rate. Although other free radicals (e.g., ·OOH) are generated, their oxidation potential was much lower than that of ·OH, resulting in the reaction was inhibited [11].

According to the results of Cu^{2+} dissolution amount (Fig. 2b), 0.04 mol/L H_2O_2 had the lowest TOC removal rate and highest Cu^{2+} dissolution amount, which was different from 0.09, 0.13 and 0.18 mol/L H_2O_2. The 0.09 mol/L H_2O_2 had the lowest Cu^{2+}dissolution amount. The addition of excess H_2O_2 had little effect on increasing in TOC removal rate. And the Cu^{2+}dissolution amount cannot be significantly reduced. Therefore, 0.09 mol/L H_2O_2 was adopted in the subsequent experiments.

The influence of different ions on the reaction

Different acid and alkali (phosphoric acid, nitric acid, hydrochloric acid, potassium hydroxide, sodium hydroxide) were added to investigate the influence of various ions (PO_4^{3-}, NO_3^-, Cl^-, K^+, Na^+) on the degradation of maleic acid and the results are shown in Fig. 3. The reaction was promoted in the presence of alkali whereas inhibited in the presence of acid. The reaction was the fastest after added potassium hydroxide. The TOC removal rate of the reaction at 2 min was 3.9 times higher than that of

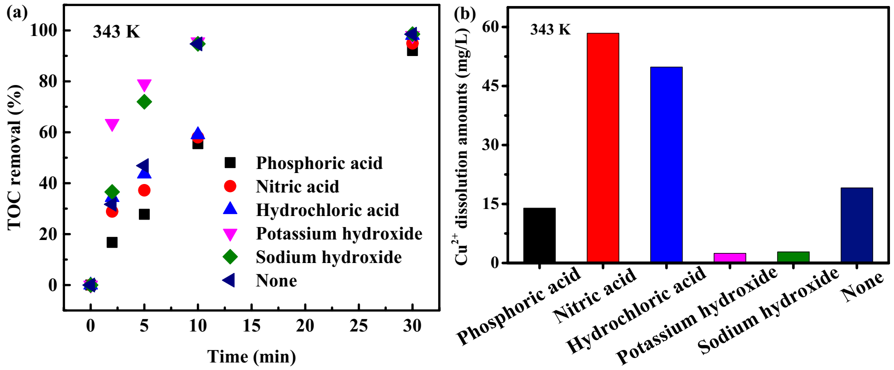

Fig. 3 The effects of various anions on the **a** TOC removal rate and **b** Cu^{2+} dissolution amounts in the catalytic wet peroxide oxidation of maleic acid. Reaction conditions: concentration of maleic acid = 500 mg/L, catalyst (5% Cu/Al_2O_3) dosage = 5 g/L, H_2O_2 dosage = 0.09 mol/L, reaction temperature = 343 K, and concentration of phosphoric acid, nitric acid, hydrochloric acid, potassium hydroxide, sodium hydroxide = 0.0025 mol/L

phosphoric acid, which having the lowest TOC removal rate. The similar results were also observed by Choi et al. [11]. The inhibitory effect of phosphoric acid was most obvious on the reaction, followed by nitric acid and hydrochloric acid.

Inorganic ions have different impact on the catalytic performance in degrading maleic acid [10]. The reaction with alkali might be promoted via the following two ways. At first, the maleic acid aqueous solution was acidic. The dissolution of Cu components will be promoted in acidic solution at the presence of H_2O_2 (See Sect. 3.1). The solution could be neutralized by the alkali, making the Cu components supported on the catalyst more stable. Because copper catalysts exhibit poor catalytic performance under acidic conditions. Secondly, cation could participate the catalytic reaction to promote the generation of ·OH in the reaction. Ni et al. reported that adding alkaline earth metals to catalyst could improve their catalytic oxidation performance [22].

The reaction with acid might be inhibited via the following two ways. First, these anions of acid might be oxidized in the presence of ·OH. For example, The Cl^- could react with ·OH to produce $ClOH\cdot^-$ (Eq. 9). The $ClOH\cdot^-$ can be further transformed to Cl· under acid conditions (Eq. 10) [23]. The reduction potential of Cl· (2.4 V) was lower than ·OH (2.8 V). The ·OH can react with PO_4^{3-} to produce $PO_4\cdot^{2-}$ (Eq. 11), The ·OH can react with NO^{3-} to produce $NO_3\cdot$ (Eq. 12). These radicals, such as Cl· and $PO_4\cdot^{2-}$, have lower reaction rate with organic compounds. Thus, the reaction with acids usually presented inhibition phenomenon compared to ·OH.

$$Cl^- + \cdot OH \rightarrow ClOH\cdot^- \tag{9}$$

$$ClOH\cdot^- + H^+ \rightarrow Cl\cdot + H_2O \tag{10}$$

$$\cdot OH + PO_4^{3-} \rightarrow PO_4\cdot^{2-} + OH^- \tag{11}$$

$$NO_3^- + \cdot OH \rightarrow NO_3 \cdot + OH^- \tag{12}$$

Second, the catalyst performance was affected by acid. The cycle of Cu(I)/Cu(II) was the key for the catalytic stability. During the process, Cu(II) can form the complexation with anions, such as phosphate ions. Thus, the amount of Cu(II) in the solution was reduced, which affected the cycle of Cu(I)/Cu(II), further affecting the catalytic performance. Compared to phosphoric acid, the removal rate of reaction with nitric acid was higher. The phosphorus with lower electronegativity in phosphoric acid is more prefer to form complexes compared to nitrogen in nitric acid. Thus, it is more difficult to form copper sulfate complexes than that of copper nitrate complexes, which can lead to a lower TOC removal rate [24]. It is worth noting that the addition of phosphoric acid did not cause a large amount of Cu^{2+} dissolution, which was not similar to hydrochloric acid and nitric acid. This phenomenon indicated that phosphoric acid mainly reduced the reaction rate through the first inhibitory effect type. During the reaction process, the PO_4^{3-} tended to react with ·OH to form $PO_4 \cdot^{2-}$, rather than formed complexes with Cu^{2+} to reduce the reaction rate. In addition, the anions ionized by short chain acids, such as maleic acid and its degradation intermediates, may also have a similar complex effect on copper ions. In conclusion, the reaction will be promoted in the presence of alkali whereas inhibited in the presence of acid.

The reusability performance of catalysts

Stability and reusability of catalysts are important evaluation indicators for industrial applications. Stability testing was performed through six cycles of maleic acid degradation with the same catalyst under the same conditions. The results are shown in Fig. 4. The TOC removal rates of the reaction catalyzed by 5% Cu/Al_2O_3 reached to 90% until 4th cycle, and less than 80% at 5th cycle. The Cu^{2+} dissolution amounts in six cycles were lower than 30 mg/L (Fig. 4b). The catalyst also exhibited good deposition properties and could be completely deposited

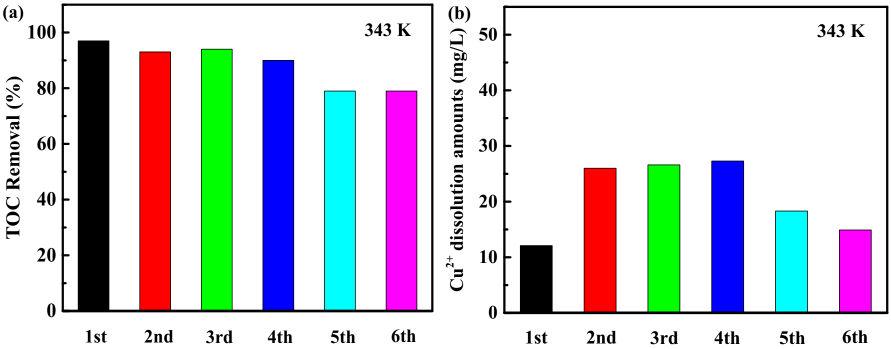

Fig. 4 The reusability of Cu/Al_2O_3 catalyst in the catalytic wet peroxide oxidation of maleic acid. **a** TOC removal rate and **b** Cu^{2+} dissolution amounts. Reaction conditions: concentration of maleic acid = 500 mg/L, catalyst (5% Cu/Al_2O_3) dosage = 5 g/L, H_2O_2 dosage = 0.09 mol/L, reaction temperature = 343 K

within a short time after stopping the agitation. Therefore, this catalyst has good practical application prospects [25].

The XRD pattern of fresh and used catalysts are shown in Fig. 5. The diffraction peaks of Al_2O_3 at 2θ of 33.3, 35.7 and 66.8° corresponded well to (107), (114) and (1114) lattice planes of aluminum oxide-Al_2O_3 (PDF-#51-0769). 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 used Cu/Al_2O_3 catalyst remained unchanged. The diffraction peaks of Cu/Al_2O_3 catalyst 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) [26, 27]. In addition, diffraction peaks of CuO and $CuAlO_2$ (PDF-#40-1037) existed in Cu/Al_2O_3 catalyst samples. And the peaks of CuO were disappeared in the pattern of 1st and 6th used catalysts samples. This difference indicated that the interaction of Cu and Al in $CuAlO_2$ was stronger than Cu and O in CuO. The results indicated that the catalyst structure was changed slightly during the reaction process. The crystal structure of the carrier remained unchanged, and the peaks of CuO was disappeared, which may be due to the loss during the reaction process and the possible transformation into other components such as $CuAlO_2$.

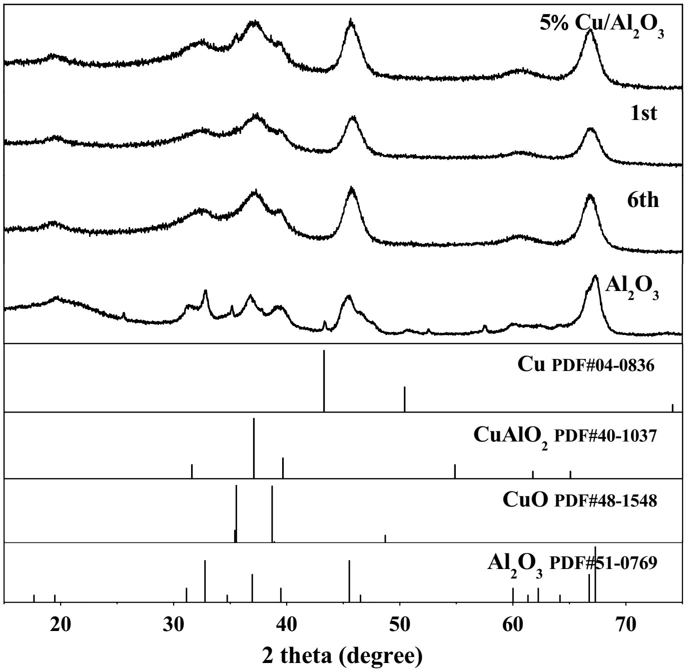

Fig. 5 X-ray diffraction of the fresh and used catalysts compared with selected standard diffraction pattern from the JCPDS card

Proposed reaction mechanism

In above sections, the effects of reaction temperature, Cu component supported amounts and H_2O_2 initial concentration on catalytic reaction rates and dissolution of the Cu component were studied (section "Optimization of catalytic reaction conditions"), and the experiments with different ions were performed (section "The influence of different ions on the reaction"). Some interesting clews have been concluded in the catalytic reaction results. Especially, the reaction was promoted in the presence of alkali whereas the reaction was inhibited in the presence of acid. To better explain the process of maleic acid degradation catalyzed by Cu/Al_2O_3 at present of different ions, the catalytic reaction mechanism was proposed, discussed and tested. The proposed reaction mechanism is summarized as follows.

The Cu component, maleic acid, H_2O_2 and different ions are involved in the proposed catalytic reaction mechanism. At first, the possible reactions between the cycle of Cu(II)/Cu(I) and H_2O_2 were discussed. H_2O_2, as an oxidant, can be converted into ·OOH and ·OH, respectively catalyzed by Cu(II) and Cu(I) [28, 29], and the valence conversion of Cu component (Cu(II)/Cu(I)) was completed in this process. Therefore, two possible reactions (Eqs. 13, 14) are included in the proposed mechanism.

$$Cu^{2+} + H_2O_2 \rightarrow Cu^+ + \cdot OOH + H^+ \tag{13}$$

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + \cdot OH + OH^- \tag{14}$$

Then the ·OH reacted with maleic acid to generate CO_2 and H_2O (Eq. 4). However, the Eq. 4 was not completed only in one step. The maleic acid was converted into short-chain acids firstly (Eq. 15) [30]. Then, the short-chain acids were further oxidized to CO_2 and H_2O. The H^+ ionized from short-chain acids that have not been degraded will contribute to form acidic solutions (Eq. 16).

$$C_4H_4O_4 + \cdot OH \rightarrow \text{short-chain acids} \tag{15}$$

$$\text{Short-chain acids} \rightarrow H^+ + ROO^- \tag{16}$$

The Cu^{2+} dissolution behavior is illustrated in the maleic acid CWPO reaction system. When the reaction temperature and concentration of H_2O_2 was higher, the TOC removal was higher. At the same time, the Cu^{2+} dissolution was lower (Fig. 1). This trend was explainable with the aid of Eqs. 4, 15, and 16 as follows. When maleic acid in the reaction solution was fully mineralized Eq. 4, the contribution of Eqs. 15–16 was relatively less. Thus, the concentration of the short-chain acids was less, and their electroionized forms was also less. The maleic acid and its degradation intermediates are important species in maintaining the system acidity, and the acidic conditions are the main reason for the large Cu^{2+} dissolution amount. Therefore, when organics was more completed degraded, the Cu^{2+} dissolution amount was lower.

Notably, the reaction rate will be changed when alkali and acids are added to the system. The reaction will be promoted in the presence of alkali whereas inhibited in the presence of acid (section "The influence of different ions on the reaction"). The reaction with alkali can be promoted in two ways. At first, the maleic acid solution could be neutralized by the alkali. The leaching amount of copper will be reduced compared to the original system, which making the Cu components supported on the catalyst more stable. Secondly, the cation may participate the catalytic reaction to promote the generation of ·OH in the reaction. The reaction with acid can be inhibited in two ways. First, these anions of acid might be oxidized in the presence of ·OH. These obtained radicals, such as Cl· and $PO_4 \cdot^{2-}$, have lower reaction rate with organic compounds than ·OH. Second, during the process, Cu(II) can form the complexation with anions, such as phosphate ions. Thus, the amount of Cu(II) in the solution will be reduced, which affected the cycle of Cu(I)/Cu(II), further affecting the catalytic performance.

In addition, H_2O_2 may not be fully converted into ·OH and accompanied with self-decomposition (Eq. 17). This process will be accelerated at higher temperature. The reactive oxidant species may be consumed by themselves (Eqs. 6–8), and the organic matters may not be oxidized.

$$H_2O_2 \rightarrow H_2O + O_2 \tag{17}$$

To better support the reaction mechanism proposed above, the TOC removal rates, Cu^{2+} dissolution and pH values during the reaction are collected in Table 1.

Due to the dissociation of H^+ by water and the acidity of the maleic acid solution (pH 2.5), a small amount of Cu^{2+} was dissolved in the solution. As soon as the H_2O_2 added, the reaction began. The short-chain acids were formed from maleic acid, which can be ionized to H^+, and then oxidized to CO_2 and H_2O. The pH value of the solution increased slightly during this process. The final pH value of the solution was remained weakly acidic because of the dissolution of refractory short-chain acids and CO_2. The Cu component participated in the redox reaction and complete valence state transitions during the reaction process. Simultaneously, the acidic solution formed from dissociation of acids, leading to large metal dissolution amount.

Table 1 The changes of pH, Cu^{2+} dissolution and TOC removal % during the reaction

Reaction time (min)	0	2	5	10	20	60
pH	2.5	2.7	3.3	3.8	6.0	6.4
Cu^{2+} dissolution amounts (mg/L)	2.0	20.4	32.5	46.1	48.6	13.5
TOC removal %	0	34	47	74	95	98

Reaction conditions: concentration of maleic acid = 500 mg/L, catalyst (5% Cu/Al_2O_3) dosage = 5 g/L, H_2O_2 dosage = 0.09 mol/L, reaction temperature = 343 K

Conclusion

In this work, different Cu/Al_2O_3 catalysts were prepared for the CWPO reaction of maleic acid. The catalytic reaction conditions were optimized and the effect of different inorganic ions on catalytic performance were investigated. The primary findings are summarized as follows.

(i) The 5% Cu/Al_2O_3 catalyst showed an excellent catalytic performance for maleic acid degradation under optimized reaction conditions. The TOC removal rates reached to 98%. At the same time, 5% Cu/Al_2O_3 catalyst maintained a lower Cu^{2+} dissolution amount during reaction.
(ii) The effect of reaction temperature on the TOC removal rate was optimum, followed by Cu component supported amounts and H_2O_2 concentrations. Acid lead to a higher TOC removal rates, while alkali had an inhibitory effect on the catalytic degradation reaction.
(iii) A catalytic reaction mechanism was proposed mainly for explanation of the effect of different inorganic ions on catalytic performance. The proposed mechanism is consistent with experimental findings.

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

Declarations

Competing interests There are no competing interests to declare.

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