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Oxidation of acetaminophen by Green rust coupled with Cu(II) via dioxygen activation: The role of various interlayer anions (CO_3^{2-}, SO_4^{2-}, Cl^-)

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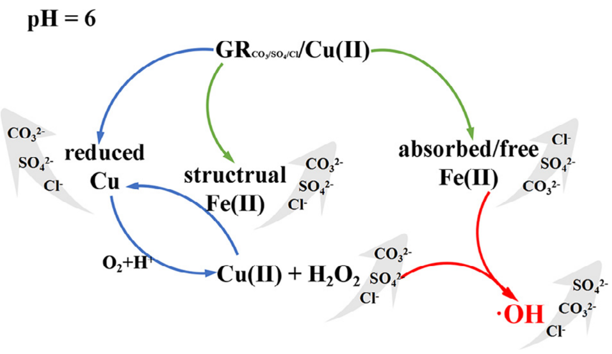
HIGHLIGHTS

- ACT was oxidized by Green Rust(GR) coupled with Cu(II).
- GR_{SO4}/Cu(II) had the greatest catalytic reactivity in the degradation of ACT.
- CO_3^{2-} affected GR_{CO3}/Cu(II)-O_2 reaction by complexing with Cu(I) and consuming·OH.
- Cl^- slowed down GR_{Cl}/Cu(II)-O_2 reaction by complexing with Cu(I).

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, three GR/Cu(II) (Green Rust/Cu(II)) composites (GR_{SO4}/Cu(II), GR_{CO3}/Cu(II), and GR_{Cl}/Cu(II)) were synthesized and used to activate dioxygen under weakly acidic conditions. The change in the mechanism caused by three interlayer anions, CO_3^{2-}, SO_4^{2-}, and Cl^-, was discussed for the first time. Both Cu(I) and H_2O_2 were generated during GR/Cu(II)-induced dioxygen activation, resulting in the rapid degradation of acetaminophen. The inconsistency between the reaction constant rates and oxidation reduction potential (ORP) order revealed the effects of the various types of interlayer ions. To further reveal the effects of the anions, the variations in the morphology and valence states of the composites were examined. To identify the rate-controlling step of dioxygen activation by the three composites, the production of reactive oxygen species (ROS) was investigated and compared. The combination of interlayer anions and metal ions changed the oxide morphology of the solid-phase materials. Furthermore, changes in the content of the reductive species (Fe(II) or Cu(I)) either enhanced or inhibited specific reaction steps. The results from this study could deepen our understanding of the effects of anions on dioxygen activation by transition metals and provide a basis for the study of oxidation reactions and mechanisms in the presence of various anions.

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1. Introduction

The activation of dioxygen has attracted considerable attention as a new advanced oxidation process (AOP) because dioxygen is a green and economical oxidizing agent, O_2. Through activation of molecular oxygen to form reactive oxygen species (ROS), the triplet state of O_2 is capable of performing spin-forbidden reactions with organics to oxidize organic contaminants. The activation of molecular oxygen usually occurs through weakening of the O=O bond and conversion of dioxygen to various ROS, such as $\cdot O_2^-$, H_2O_2, and $\cdot OH$, of which $\cdot OH$ is the major product. Two mechanisms of molecular oxygen activation are possible, namely, one-electron reduction (Eqs. 15) and two-electron reduction (Eqs. (6) and (7)) [1–3]. The O_2 activation pathway is determined by the molar ratio between the O_2 molecules and oxygen vacancies. When the ratio of O_2 molecules to the surface oxygen vacancies is 1:1, two-electron transfer occurs, producing an O_2^{2-} species with an O-O bond length of 1.46 Å. When the ratio is greater than 1:1, the surface is covered with elevated levels of O_2. Under such conditions, one-electron transfer occurs, generating $\cdot O_2^-$ with an O—O bond length of 1.33 Å [4,5].

One-electron reduction:

$$O_2\ e^- \rightarrow \cdot O_2^- \tag{1}$$

$$\cdot O_2^- + 2H^+ + e^- \rightarrow H_2O_2 \tag{2}$$

$$2\ \cdot O_2^- + 2H^+ + e^- \rightarrow H_2O_2 + O_2 \tag{3}$$

$$H_2O_2 + H^+ + e^- \rightarrow \cdot OH + H_2O \tag{4}$$

$$H_2O_2 \rightarrow \cdot OH + OH^- \tag{5}$$

Two-electron reduction:

$$O_2 + 2e^- \rightarrow O_2^{2-} \tag{6}$$

$$O_2^{2-} + 2H^+ \rightarrow H_2O_2 \tag{7}$$

Various catalyst materials have been developed to activate dioxygen, including biomimetics, photocatalysts, and transition metals. Both zero-valent iron (ZVI) and zero-valent aluminium (ZVAl) were reported to be able to activate dioxygen, however having rather low activating efficiency for the invalid consumption of electrons. [6–8]. Among them, Cu is an ideal catalyst that exhibits high reactivity in the activation of molecular oxygen (Eqs. (8) and (9)) [9–12].

$$Cu^+ + O_2 \rightarrow Cu^{2+} + \cdot O_2^- \tag{8}$$

$$Cu^+ + \cdot O_2^- + 2H^+ \rightarrow Cu^{2+} + H_2O_2 \tag{9}$$

During the activation of O_2, Cu(I) plays an essential role in the transformation of $\cdot O_2^-$ to H_2O_2 [13–15]. The $\cdot O_2^-$ produced reacts rapidly with Cu(I) to produce H_2O_2 at a rate in the range of $1.98–9.4 \times 10^9\ M^{-1}\ s^{-1}$ (Eq. (9)) [10,12]. Therefore, to increase the reactivity of Cu in O_2 activation, increasing the content of Cu(I) both in solution and on the catalyst surface is crucial.

Although Cu(I) exhibits high reactivity in O_2 activation, its slow regeneration from Cu(II) greatly limits the application of Cu. Therefore, methods for accelerating the cycling of Cu(II)/Cu(I) to improve the catalytic efficiency of Cu are necessary. In our previous studies, green rust (GR) composites with high reducibility can transform Cu(II) to Cu (I) under neutral pH conditions [16]. Thus, the design of a GR/Cu(II) system for O_2 activation is feasible. In such a system, Cu(II) is reduced in situ to Cu(I), which then activates O_2 to generate ROS. GR typically contains structural Fe(II) and Fe(III) in a layered bimetallic structure. Its crystal structure is made up of alternating layers of positively charged hydroxides, $[Fe^{II}_{1-x}\,Fe^{III}_x\,(OH)_2]^{x+}$ [17], and negatively charged anions, A^{n-}, as interlayer anions; these anions are commonly CO_3^{2-}, SO_4^{2-}, and Cl^- [18]. Thus, GR can be divided into three categories: GR_{CO3}, GR_{SO4}, and GR_{Cl}. Studies have previously demonstrated the high reactivity of GR and particularly its high activity in the reductive degradation of nitrate, chromate, and halogenated hydrocarbons [19–22]. Therefore, the cycling of Cu(II)/Cu(I) can be accelerated by introducing GR into a Cu(II) system to enhance the concentration of Cu (I).

The reducibility of GR mainly depends on the structural Fe(II) hydroxides [23–25]. Compared with Fe(II) solution or nZVI, with part of Fe(II) oxidized in GR structure, the original hydrogen oxide layer will convert from electrical neutral state to positive charge. With interlayer anions inserting, the charge is balanced. Thus, GR has strong adsorption energy and can reduce anion concentration in the solution. When GR coexists with Cu(II), Cu(II) can be reduced to Cu(I) by Fe(II) at a rate of $4.2 \times 10^3\ M^{-1}\ s^{-1}$, which is several orders of magnitude faster than the reaction between O_2 and Fe(II) ($0.37\ M^{-1}\ s^{-1}$) [26]. Thus, in GR/Cu(II) system which Cu(II) and Fe(II) both exists, Fe(II) is more likely to reduce Cu(II) rather than oxidized by O_2, while Cu(I) played a major role in activating O_2. Both Cu(I) and Fe(II) can react with H_2O_2 to produce $\cdot OH$. However, the reaction rate between Fe(II) and H_2O_2 (pH = 6.5, $1.72 \times 10^3\ M^{-1}\ s^{-1}$) [26] is much faster than that between Cu(I) and H_2O_2 ($< 100\ M^{-1}\ s^{-1}$) [27,28]. Therefore, Fe(II) not only is the reductant of Cu(II), but the catalyst of H_2O_2 to produce $\cdot OH$ as well. By introducing Cu(II) into GR, Cu(II) is reduced in situ to Cu(I), which results in a great reactivity in activating dioxygen reaction. Meanwhile, GR is oxidized to goethite (α-FeOOH) and magnetite (Fe_3O_4) [29]. Therefore, the Fe(II) species in the GR/Cu(II) composite plays two important roles: reducing Cu(II) to Cu(I) under weakly acidic conditions and producing $\cdot OH$ from the reaction with H_2O_2, which is generated via the activation of O_2 by Cu(I) (Eqs. (8) and (9)).

The interlayer anions of GR influence its adsorption properties and redox reactivity. However, no research has been reported regarding the effects of different interlayer anions on the reactivity of GR/Cu(II) composites toward O_2 activation. In this research, GR/Cu(II) composites were prepared in a similar method as that developed for the preparation of GR. In the resulting GR/Cu(II) composites, the anions may significantly change the oxidation ability and mechanism of the AOPs by attaching to the catalyst surface and affecting the generation of free radicals, as they do in GR. As has been reported, changing the specific surface area of GR causes the adsorption rate of monovalent anions by to be faster than that of divalent anions [30]. The efficiency of nitrate reduction by monovalent anionic GR (GR_F and GR_{Cl}) is higher than that by divalent anionic GR (GR_{CO3} and GR_{SO4}) because the Fe(II)/Fe(III) ratio is higher in the former, and Fe(II) is the active species [31]. Furthermore, the removal efficiency of chromate by GR is affected not only by the GR interlayer spacing, as interlayer ion exchange may occur [32], but also by the reaction position, which is determined by the anions [33]. The interlayer ions can be inferred to have similar influences in GR/Cu(II) composites as they do in GR. Both the crystal structure and the reaction of Fe(II) and Cu(II) can be affected by the type of interlayer anions, which can further affect the activity of the composite.

In this research, highly active GR/Cu(II) composites were synthesized and used to activate dioxygen under weakly acidic conditions (pH = 6). Three GR/Cu(II) composites (GR_{SO4}/Cu(II), GR_{CO3}/Cu(II), and GR_{Cl}/Cu(II)) were compared to examine two particular questions: (a) how are the Cu(I) and Fe(II) contents and structural morphology related to the type of interlayer anions, and (b) how is ROS generation affected by the interlayer anions? This study revealed that the various interlayer ions had different effects on the GR/Cu(II) reaction rate, the mechanism by which the three composites activated O_2 was explained. The study provides a basis for studying oxidation reactions and mechanisms in the presence of various anions and offers new ideas for the construction of GR/metal materials.