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Catalytic activities of dissolved and Sch-immobilized Mo in H_2O_2 decomposition: Implications for phenol oxidation under acidic conditions

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ABSTRACT

Schwertmannite (Sch), a good geo-sorbent for immobilizing molybdate oxyanion in natural environment, has been used as an efficient Fenton-like catalyst in the remediation of organic pollutants. However, what's the influence of immobilized molybdate (Mo_{imm}) on the catalytic activity of Sch and what's the catalytic difference between Mo_{imm} and dissolved molybdate (Mo_{diss}) in H_2O_2 activation are still unknown. In this study, we first find a dual mechanism of Mo-Sch involved in phenol oxidation. At low Mo_{imm} loadings (0.01Mo-Sch and 0.05Mo-Sch), phenol oxidation is predominantly mediated by $HO^\bullet$ radicals generated from dissolved Fe(III) or surface ≡Fe(III) on Sch, whereas at high loadings (1Mo-Sch and 10Mo-Sch), $^\bullet OOH$ as well as $^1O_2$ generated from monomeric Mo complexes on Sch under acidic conditions also play important roles in phenol oxidation. Unlike Mo-Sch, Mo_{diss} forms dimeric $Mo_2O_3(O_2)_4{}^{2-}$ with H_2O_2 under acidic conditions, which can oxidize phenol directively or via $^\bullet OOH$ radicals, generated from dissolved $Mo_2O_3(O_2)_4{}^{2-}$. The dimerization of Mo_{diss} with H_2O_2 inhibits $^1O_2$ generation. During the experiments, Mo_{diss} can also interfere with the chain reactions between dissolved Fe(III) and H_2O_2, accelerating H_2O_2 decomposition via an O_2 generation pathway, which significantly reduces the utilization efficiency of H_2O_2 in phenol oxidation.

1. Introduction

Hydrogen peroxide (H_2O_2) is a strong oxidant (E_0 = 0.87–1.80 V) that is extensively used for the oxidation of various organic pollutants. It can be decomposed via different pathways and generates various oxidative radicals such as hydroxyl radicals ($HO^\bullet$), superoxide radicals ($^\bullet OOH/O_2{}^{-\bullet}$), singlet oxygen ($^1O_2$), or forms oxidative species with transitional metals such as TAML [1–3]. Among all these radicals, $HO^\bullet$ radicals generated from Fenton or Fenton-like reactions can non-selectively degrade organic contaminants to smaller molecules or CO_2. Our recent study suggested that schwertmannite (Sch), an Fe(III)-oxyhydroxysulfate mineral, exhibited an excellent catalytic activity in the degradation of phenol by activating H_2O_2 via a $HO^\bullet$ pathway [4]. Large quantities of $HO^\bullet$ radicals generated from dissolved or immobilized Fe(III) on Sch can completely oxidize phenol in a short time under acidic conditions [4]. Recently, Duan et al. [5] also pointed out that $HO^\bullet$ generated from the activation of H_2O_2 by Sch contributed to 92.5% removal of nitrobenzene within 30 min at pH 3.0.

Dissolved molybdate (Mo_{diss}) is an interesting oxyanion that can be transformed by H_2O_2 to various monomeric peroxomolybdates, such as $MoO_3(O_2)^{2-}$, $MoO_2(O_2)_2{}^{2-}$, $MoO(O_2)_3{}^{2-}$ and $Mo(O_2)_4{}^{2-}$ via Eq. (6) or a tetraperoxodimolybdate, $Mo_2O_3(O_2)_4{}^{2-}$ via Eq. (5) [6–8]. In the pH range of 2.5–5.0, $Mo_2O_3(O_2)_4{}^{2-}$ is a predominant Mo species and plays an important role in epoxidation of olefins and alcohols [6,7,9]. Under alkaline conditions, $MoO_3(O_2)^{2-}$, $MoO_2(O_2)_2{}^{2-}$, $MoO(O_2)_3{}^{2-}$ and $Mo(O_2)_4{}^{2-}$ are predominant species and can evolve $^1O_2$ (Eq. (1)) to effectively

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peroxidize organics [7,10,11]. Sels et al. [9,12] further pointed out that only monomeric Mo on layered double hydroxides (LDHs) could accelerate the generation rate of $^1O_2$ under alkaline conditions, and the amount of $^1O_2$ in Mo-LDHs system was only half of that generated in the Mo_{diss} system. However, what's the catalytic activity of Mo-LDHs under acidic conditions has not been investigated due to the easy dissolution of LDHs at low pHs.

$$2H_2O_2 \xrightarrow[\text{pH } 9-12]{MoO_4{}^{2-}} 2H_2O + {}^1O_2 \quad (1)$$

In natural environments, molybdate is always associated with Sch or other iron (oxyhydr) oxides in tailings and AMD from the molybdenite [13–16]. Yager et al. [13] found that Mo concentrations in soil on the Mount Moly, Silverton, Colorado, U.S. always ranged from 2 to 1700 mg g^{-1} soil, and X-ray diffraction (XRD) analysis confirmed the occurrence of Sch in the debris fans. In addition, Hayes et al. [14] noticed that molybdate precipitated as ferrimolybdite [$Fe_2(MoO_4)_3 \cdot 8H_2O$] or was adsorbed on ferrihydrite [$MoO_4{-}Fe(OH)_3$] during tailing preparation processes. Given the high specific surface area, Sch shows a high adsorption capacity to molybdate, with a maximal adsorption capacity of 115 mmol $MoO_4{}^{2-}$ mol^{-1} Fe at pH 4.5 [17]. Similar ionic radius and charge of molybdate with $SO_4{}^{2-}$ also facilitate it to exchange with the adsorbed or the structural $SO_4{}^{2-}$ in Sch [17,18].

Owing to the close geochemical relationships between Mo and Sch, it is necessary to consider the influence of Mo on the catalytic activity of Sch in Fenton-like reactions. To the best of our knowledge, the presence of Mo on the catalytic activity of iron oxides during Fenton-like reactions has not been reported. In addition, mechanisms involved in H_2O_2 decomposition catalyzed by Sch immobilized Mo (Mo-Sch) and Mo_{diss} may be different under acidic conditions, given that $HO^\bullet$ radicals generated from Sch may interfere with activation of H_2O_2 by Mo_{imm}. In this study, catalytic activity of Mo_{diss} and Mo-Sch in H_2O_2 activation under acidic conditions will be compared in the oxidation of phenol, a highly toxic contaminant which poses serious threats to human health and our environment [19,20]. Mechanisms of H_2O_2 activation involved in these processes will also be explored.

2. Experimental

2.1. Chemicals

All chemicals were of analytical grade or higher purity, and all solutions were prepared in deionized water. $Fe_2(SO_4)_3$ and *tert*-butanol were obtained from Tianjin Bodi Chemical Co. Ltd., $NaH_2AsO_4.7H_2O$ was purchased from Merck, and Na_2MoO_4, 38% HCl, 98% H_2SO_4, 30% H_2O_2, NaOH and phenol were purchased from Tianjin Bei Fang Chemical Co. Ltd.

2.2. Methodology

2.2.1. Preparation of Sch and Sch-Mo and phenol oxidation experiments

Freeze-dried Sch [$Fe_8O_8(OH)_{8-2x}(SO_4)_x$, $1 \le x \le 1.75$] was prepared according to the method described previously [4]. Sch-Mo was prepared by dispersing 0.15 g freeze-dried Sch in 100 mL deionized water for 2 h. A measured amount of concentrated molybdate stock was then added into the suspension, with a final working volume of 150 mL. pH was then adjusted to 3.0 by 1.0 M HCl or NaOH. Samples were then placed on a shaker at 150 rpm and 25 °C for 24 h to reach adsorption equilibrium. After that, Sch-Mo was centrifuged and re-dispersed in 100 mL deionized water with the pH of 3.0. Sch after the addition of 0.01–10 mM molybdate are named after 0.01Mo-Sch, 0.1Mo-Sch, 1Mo-Sch, etc. The suspension was subsequently mixed with a 50 mL phenol solution with the pH of 3.0. Oxidation of phenol was initiated with the addition of a measured amount of 30% H_2O_2. The experiments were carried out in dark to avoid possible photochemical reactions involved in oxidation processes. Initial concentrations of H_2O_2 and phenol were always controlled at 500 and 100 mg L^{-1}, respectively. The flasks were then placed on a shaker with a rotation speed of 150 rpm, and 4 mL sample was regularly taken out and centrifuged at 10,000 rpm for 5 min. Concentrations of H_2O_2, phenol, dissolved molybdate and Fe in the supernatant were then measured. All experiments were conducted in duplicate at 25 °C and the average values were recorded.

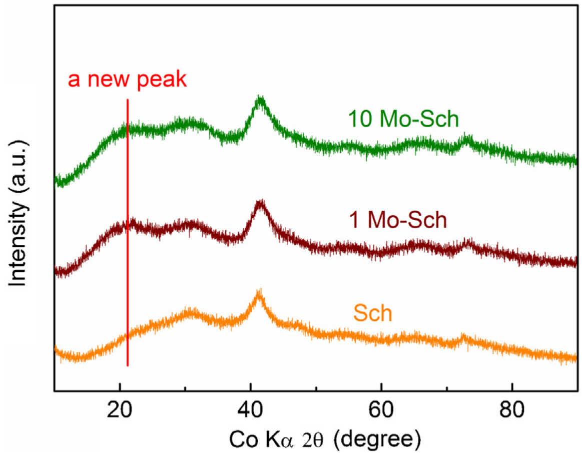

Fig. 1. XRD analysis of Sch Mo-Sch. Initial concentration of Sch was 1 g L^{-1} with a working volume of 150 mL after 24 h.

2.2.2. Analytical methods

The 4-aminoantipyrine method was used for the measurement of phenol concentration [21], and the detection limit was 0.1 mg L^{-1} as determined in our previous study [4]. Concentration of H_2O_2 was determined by a titanium sulfate method [22]. Inductively Coupled Plasma (ICP, Varian 715S) was also employed to determine dissolved Fe and molybdate.

The morphology of Sch and Sch-Mo was examined by a high-resolution TEM (JEM-2100F, JEOL). The crystalline structure of the synthetic Sch and Mo-Sch were characterized by XRD (D/Max-2500, Rigaku) with a Co X-ray source ($\lambda = 1.7902$ Å). Samples were scanned from $2\theta = 10$–$90°$ with a $2\theta = 0.02°$ step-size. EPR spin trapping analysis was performed on a Bruker EMX 10/12 spectrometer with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as a spin-trapping agent. Surface properties of Mo-Sch were characterized with a Thermo Nicolet Nexus FTIR spectrometer via a KBr pressed disk.

3. Results and discussion

3.1. Characterization of Sch and Mo-Sch

Characteristic peaks of the synthesized Sch agree well with the standard Sch card (Fig. 1, PDF 47-1775), and the Fe oxyhydroxide displays a needle-like morphology with a diameter of ca. 100 nm (Fig. 2a). ICP analysis indicates a formula of $Fe_8O_8(OH)_{4.5}(SO_4)_{1.75}$ of this Sch. FTIR spectrum exhibits characteristic —OH deformation (δ_{OH} at 860 and 712 cm^{-1}) and stretching (ν_{OH} at 3300 cm^{-1}) vibrations of Sch (Fig. 3). The typical S—O stretching (ν_{SO}) modes consist of a broad ν_3 band at 1120, 1190 and 1030 cm^{-1}, a ν_1 fundamental of the symmetric $SO_4{}^{2-}$ stretch at 985 cm^{-1}, and a ν_4 bending band at 610 cm^{-1} (Fig. 3) [23].

XRD analysis of Sch-Mo shows a more intense peak at 41.80° in 1Mo-Sch and 10Mo-Sch, implying that high concentrations of Mo_{imm} enhance the crystalline degree of Sch (Fig. 1). Previous stud-