



Highly active iron-containing silicotungstate catalyst for heterogeneous Fenton oxidation of 4-chlorophenol



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ARTICLE INFO

Article history:

Received 4 January 2015

Received in revised form 23 May 2015

Accepted 25 May 2015

Available online 27 May 2015

Keywords:

Polyoxometalate

Silicotungstate

Heterogeneous catalysis

Fenton oxidation

4-Chlorophenol

ABSTRACT

Polyoxometalates (POMs) have been a class of attractive redox catalysts and photocatalysts, but so far, there have been few reports on application of POMs in Fenton (or Fenton-like) oxidation processes. In this context, an iron-containing silicotungstate ($\text{Fe}^{\text{III}}\text{AspSiW}$) was synthesized using ferric chloride (FeCl_3 , Fe^{III}), aspartic acid ($\text{C}_4\text{H}_7\text{NO}_4$, Asp) and silicotungstic acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$, SiW) as raw materials and employed as a heterogeneous catalyst for Fenton oxidizing 4-chlorophenol (4-CP). The chemical formula of $\text{Fe}^{\text{III}}\text{AspSiW}$ is speculated as $[\text{Fe}(\text{C}_4\text{H}_5\text{NO}_4)]_{3.5}\text{H}_{0.5}\text{SiW}_{12}\text{O}_{40}\cdot 14\text{H}_2\text{O}$ with Keggin-structured $\text{SiW}_{12}\text{O}_{40}^{4-}$ anion. The $\text{Fe}^{\text{III}}\text{AspSiW}$ catalyst showed high activity for oxidation of 4-CP by H_2O_2 ranging from acidic to circumneutral pHs under both the dark and irradiated conditions. Besides, the catalyst also exhibited good regenerability without significant performance drop. The catalytic mechanism in non-irradiated system was related to the Fenton-like catalysis of ferric iron in $\text{Fe}^{\text{III}}\text{AspSiW}$. Moreover, the enhanced degradation of 4-CP under irradiation was attributed to the synergistic effect of Fenton-like catalysis of ferric iron and photocatalysis of $\text{SiW}_{12}\text{O}_{40}^{4-}$ anions in $\text{Fe}^{\text{III}}\text{AspSiW}$.

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1. Introduction

Advanced oxidation processes (AOPs) based on in-situ generation of highly reactive hydroxyl radicals are known for their capability to mineralize a wide range of organic pollutants [1–3]. Among the AOPs, Fenton process using the mixture of hydrogen peroxide (H_2O_2) and ferrous iron (Fe^{2+}) for environmental remediation has been intensively studied for several decades [4–8]. However, the traditional homogenous Fenton system ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) containing a high concentration of ferrous salt as the catalyst which is usually well-functional under acidic conditions only, and massive iron sludge consisting of $\text{Fe}(\text{OH})_3$ produced during the process needs to be further disposed. Therefore, development of solid state catalysts is a promising alternative to overcome these barriers of application. Many iron-based materials such as zero-valent iron (ZVI) [9,10], S-doped $\alpha\text{-Fe}_2\text{O}_3$ [11], activated carbon/Fe [12], Fe_3O_4 magnetic nanoparticles [13], Fe_3O_4 -multi-walled carbon nanotube [14], BiFeO_3 [15] and $\text{Fe}_2(\text{MoO}_4)_3$ [16] have been reported as the

heterogeneous Fenton-like catalysts. However, many of these heterogeneous catalysts still work under acidic conditions only, and some of them exhibit marked performance drop in successive batches of contaminant degradation.

Polyoxometalates (POMs) have been a class of attractive redox catalysts and photocatalysts owing to their ability to undergo multi-electron redox reaction reversibly [17,18], but so far, there have been few reports on application of POMs in Fenton (or Fenton-like) oxidation processes. Lee and Sedlak found that $\text{PW}_{12}\text{O}_{40}^{3-}$ in homogeneous $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system could significantly enhance the oxidation of organics even at pH 8.5 [19]. Choi et al. proposed that $\text{PW}_{12}\text{O}_{40}^{3-}$ and $\text{SiW}_{12}\text{O}_{40}^{4-}$ in $\text{Fe}^0/\text{POM}/\text{O}_2$ system could mediate electron transfer from Fe^0 to O_2 to produce H_2O_2 in situ, which eventually led to the generation of hydroxyl radicals [20]. However, the water-soluble POMs used in these processes could not be recovered easily after reaction.

Our group has been working on exploring various water-insoluble iron-containing POMs as heterogeneous Fenton-like catalysts for years. We have recently demonstrated a novel Fe^{III} -containing phosphotungstate catalyst for efficiently oxidizing 4-chlorophenol (4-CP) ranging from acidic to circumneutral pHs [21]. To deepen the understanding of the catalysis of this kind of POMs in heterogeneous Fenton-like processes, exploring

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series of iron-containing POMs with different organic ligands and heteropolyanions is needed. In this work, a new Fe^{III}-containing silicotungstate (Fe^{III}AspSiW) was synthesized using ferric chloride (FeCl₃, Fe^{III}), aspartic acid (C₄H₇NO₄, Asp) and silicotungstic acid (H₄SiW₁₂O₄₀·xH₂O, SiW) as raw materials, and used as heterogeneous catalyst to degrade 4-CP in Fe^{III}AspSiW/H₂O₂ system. The catalytic mechanism was preliminarily studied.

2. Materials and methods

2.1. Reagents

Ferric chloride hexahydrate, aspartic acid, silicotungstic acid and hydrogen peroxide (30 wt.%) were provided by Sinopharm Chemical Reagent Beijing Co., Ltd. 4-CP was obtained from Tianjin Guangfu Fine Chemical Industry Research Institute. All the reagents were of analytical grade and used without further purification.

2.2. Preparation and characterization of Fe^{III}AspSiW

The synthesis of Fe^{III}AspSiW was carried out at ambient temperature. Ferric chloride hexahydrate (0.540 g) and aspartic acid (0.266 g) were firstly added in water (50 mL) with vigorous stirring for 1 h to form a soluble ferric aspartate complex. A silicotungstic acid solution (25 mL, 0.02 mol L⁻¹) was then added dropwise. After 2 h of stirring, the resulted pale yellow Fe^{III}AspSiW precipitate was centrifuged and washed with water. Finally, Fe^{III}AspSiW powder was obtained by drying the precipitate at 50 °C in vacuum.

Inductively coupled plasma atomic emission spectrometry (ICP-AES, Shimadzu ICPS-7510), thermogravimetry (TG, Seiko TG/DTA6300), Fourier transform infrared spectrometry (FT-IR, Shimadzu IRAffinity-1), UV-vis diffuse reflection spectrometry (UV-vis DRS, Shimadzu UV-2550), X-ray diffraction (XRD, XD-2, Cu K α radiation), and field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) were performed to characterize the resultant Fe^{III}AspSiW catalyst.

2.3. Catalytic degradation of 4-CP

The catalytic activity of Fe^{III}AspSiW was evaluated by degradation of 4-CP in Fe^{III}AspSiW/H₂O₂ system at 25 ± 2 °C. All the experiments were carried out in the dark and under irradiation, separately. A 400 W high pressure mercury lamp ($\lambda_{\text{max}} = 365 \text{ nm}$) was used as the source for irradiation, and the light flux at the liquid level was measured to be ca. 450 $\mu\text{W cm}^{-2}$. The experiments were carried out in a 200 mL batch quartz reactor with a recirculation circuit for temperature control. In a typical procedure, Fe^{III}AspSiW catalyst was added into 100 mL 4-CP solution (100 mg L⁻¹) with magnetic stirring to maintain a uniform suspension. The initial pH of the suspension was adjusted to a certain value using dilute aqueous H₂SO₄ or NaOH solution. After 30 min of stirring in the dark for adsorption of 4-CP to reach equilibrium, the reaction was timed with addition of H₂O₂ solution. Samples were taken at regular time intervals and analyzed immediately after filtration through a 0.22 μm filter to remove the Fe^{III}AspSiW particles. Experiments were carried out in triplicate, and the results were expressed as a mean value.

2.4. Analytical methods

The concentration of 4-CP was analyzed using a high performance liquid chromatograph (HPLC, Shimadzu LC-20AD) equipped with a C18 reverse phase column and an UV detector. The mobile phase was a mixture of methanol (65%) and 1% of acetic acid aqueous solution (35%) at the flow rate of 0.5 mL min⁻¹. Total organic

carbon (TOC) was determined by a TOC analyzer (Shimadzu TOC-V CPH).

3. Results and discussion

3.1. Characterization of Fe^{III}AspSiW

The chemical formula of Fe^{III}AspSiW is speculated to be [Fe(C₄H₅NO₄)]_{3.5}H_{0.5}SiW₁₂O₄₀·14H₂O according to ICP-AES and TG analyses. The molar ratio of Fe:Si:W in Fe^{III}AspSiW is 3.4:0.96:12 based on the ICP-AES data. The TG curve of Fe^{III}AspSiW in Fig. 1(a) shows a two-step of weight loss from ca. 30 to 420 °C. The weight loss of 6.4% from ca. 30 to 150 °C is attributed to the removal of H₂O molecules (calculated value 6.7%), and the weight loss of 12.4% from ca. 150 to 420 °C is ascribed to the decomposition of aspartate unit (calculated value 12.1%).

The FT-IR spectra are presented in Fig. 1(b). It is noticeable that H₄SiW₁₂O₄₀·xH₂O shows four fingerprint peaks of Keggin structure at 980, 926, 880 and 775 cm⁻¹, attributing to $\nu_{\text{as}}\text{W}=\text{O}_d$, $\nu_{\text{as}}\text{Si}-\text{O}_a$, $\nu_{\text{as}}\text{W}-\text{O}_b-\text{W}$ and $\nu_{\text{as}}\text{W}-\text{O}_c-\text{W}$ of SiW₁₂O₄₀⁴⁻ anion [22]. Similar vibration absorptions could be found in Fe^{III}AspSiW sample, suggesting that the Keggin-structured SiW₁₂O₄₀⁴⁻ anion is remained in Fe^{III}AspSiW. Red and blue shifts of the peaks in Fe^{III}AspSiW sample may be ascribed to the interaction between SiW₁₂O₄₀⁴⁻ anion and Fe^{III}Asp complex unit.

The UV-vis DRS of H₄SiW₁₂O₄₀·xH₂O and Fe^{III}AspSiW are presented in Fig. 1(c). It can be seen that H₄SiW₁₂O₄₀·xH₂O shows a wide absorption band in the range from 200 to 450 nm with the peaks at 210 and 265 nm, which are attributed to charge-transfer from O²⁻ to W⁶⁺ in SiW₁₂O₄₀⁴⁻ at W=O and W-O-W bonds, respectively [23]. Fe^{III}AspSiW exhibits the similar absorption band, also confirming the existence of Keggin-structured SiW₁₂O₄₀⁴⁻ unit in Fe^{III}AspSiW. It is noteworthy that Fe^{III}AspSiW shows an obvious red-shift of the absorption onset comparing with H₄SiW₁₂O₄₀·xH₂O, which may be advantageous for its photocatalysis because of the relatively narrow band gap.

XRD patterns in Fig. 1(d) show that the prepared Fe^{III}AspSiW is amorphous, while H₄SiW₁₂O₄₀·xH₂O is well crystalline. SEM image of Fe^{III}AspSiW in Fig. 1(e) displays that the sample appears to be the aggregation of irregular particles with the size of 100–150 nm.

3.2. Catalytic performance of Fe^{III}AspSiW

The catalytic performance of Fe^{III}AspSiW was tested via the degradation of 4-CP (100 mg L⁻¹) in Fe^{III}AspSiW/H₂O₂ system at 25 ± 2 °C. The initial H₂O₂ concentration and the catalyst dosage were 20 mmol L⁻¹ and 0.2 g L⁻¹, respectively. The experiments were carried out at pH 6.5, the natural pH of 100 mg L⁻¹ 4-CP solution.

Control experiments demonstrated that the removal of 4-CP with the catalyst alone or H₂O₂ alone could be neglected both in dark and irradiated systems within the observed time, compared with that caused by oxidation process in the later experiments.

As shown in Fig. 2, Fe^{III}AspSiW catalyst exhibits high activity for oxidizing 4-CP, and the catalytic activity is significantly enhanced under irradiation. The time required for complete depletion of 4-CP in the dark was ca. 30 min, while it reduced to ca. 20 min under irradiation. The TOC analysis (inset in Fig. 2) revealed similar feature. The TOC removal was ca. 93.6% within 3 h of irradiation, and it was ca. 91.0% within 6 h of reaction in the dark.

The regenerability of catalyst was tested under the same conditions. As shown in Table 1, the catalytic behavior of Fe^{III}AspSiW is reproducible in consecutive experiments without a remarkable drop in the process efficiency. The characteristic infrared absorption bands of Keggin structure in recycled Fe^{III}AspSiW (Fig. 1(b))

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