



Visible-light-driven selective oxidation of alcohols using a dye-sensitized TiO₂-polyoxometalate catalyst



Xue Yang^{a,b}, Hui Zhao^{a,b}, Jifei Feng^a, Yanning Chen^{a,b}, Shuiying Gao^{a,*}, Rong Cao^{a,b,*}

^a State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China

^b College of Chemistry, Fuzhou University, Fuzhou 350002, China

ARTICLE INFO

Article history:

Received 10 January 2017

Revised 22 March 2017

Accepted 23 March 2017

Keywords:

Photo-oxidation

Alcohol

Visible light

TiO₂

Dye

Polyoxometalate

ABSTRACT

This study demonstrated a dye-sensitized TiO₂-polyoxometalate system (denoted TiO₂-(PW₁₂-TH)₈, where PW₁₂ = PW₁₂O₄₀³⁻ and TH = thionine) for selective oxidation of alcohols under visible light. The results showed that various substituted alcohols were transformed into their corresponding aldehydes with high selectivity. Due to more efficient electrons transfer, large surface area, and enhanced visible light absorption, the photocatalytic activity of TiO₂-(PW₁₂-TH)₈ was superior to any other dye-sensitized system reported to date. The response in the photocurrent-time curves over several on/off cycles of intermittent irradiation showed good reproducibility. The photocurrent response of TiO₂-(PW₁₂-TH)₈ was much higher than that of TiO₂/TH (physical mixture of TiO₂ and TH), SiO₂-(PW₁₂-TH)₈ or P25-(PW₁₂-TH)₈ (P25 = Degussa P25), attributed to the more efficient transfer and longer lifetime of photoexcited electrons. This photocatalytic process confirmed that efficient electron transfer during photocatalytic oxidation plays a vital role in determining the reaction conversion and obtaining good selectivity. Electron paramagnetic resonance (EPR) spectra and radical scavenging experiments proved that superoxide radicals and electrons were the main reactive species in the proposed system, the absence of hydroxyl radicals and holes is demonstrated to be the key of high reaction selectivity.

© 2017 Elsevier Inc. All rights reserved.

1. Introduction

The selective oxidation of alcohols has received considerable attention in both industrial manufacturing and organic syntheses [1,2]. The photo-assisted transformation of alcohols, which can be conducted under visible light irradiation, has especially attracted growing interest due to its promising potential for solar energy utilization [3–5]. In addition, compared with conventional industrial oxidation processes, over-oxidation can be avoided in photocatalysis [6–8]. Various semiconductor metal oxides have been used in selective photo oxidation reactions, but TiO₂ is the most reliable material for green chemistry and energy sustainable solutions, mainly due to two apparent advantages: (1) TiO₂ is abundant, stable and easy to prepare and (2) TiO₂ possesses appropriate redox potentials for its conduction band (CB) and valence band (VB) to ensure the reduction of O₂ and oxidation of H₂O or organic compounds simultaneously [9–12]. However, the large band gap of TiO₂ (Eg > 3.0 eV) greatly impedes its application in

visible light photocatalysis and fast electron-hole recombination typically results in poor selectivity of the products [13,14]. To address this concern, many approaches have been proposed that include compositing TiO₂ with other materials to increase the light response region [15], doping TiO₂ with metal ions or non-metal ions [16–18], incorporating carbon nanotubes into TiO₂ [19], supporting photocatalysts on graphene with large surface area, combining TiO₂ with other narrow band gap semiconductors to form heterojunctions [20–22] or sensitizing with dyes [23]. However, these doping processes may reduce the redox potential of photoelectrons or photoholes and lead to lower photocatalytic activity. Li et al. showed that Pd-loaded anatase TiO₂ nanotubes have excellent visible light photoactivity in the photocatalytic oxidation of propylene [24]. However, the use of noble metal is relatively expensive and could potentially generate abundant amounts of heavy metal waste. These processes have been challenged recently by a promising strategy. Many of the processes include dyes or other colored species adsorbed on the surface of TiO₂ to improve its photocatalytic activity under visible light by enhanced light absorption [25–27]. Zhao's group investigated the aerobic selectivity in the oxidation of alcohols to aldehydes upon visible light irradiation using a coupled system consisting of dye alizarin red-sensitized TiO₂ and TEMPO [28]. Hydroxyl radicals (·OH) are

* Corresponding authors at: State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China. Fax: +86 591 83796710 (R. Cao).

E-mail addresses: gaosy@fjirsm.ac.cn (S. Gao), rcao@fjirsm.ac.cn (R. Cao).

generally regarded as “non-selective” radical species in otherwise “selective” oxidation reactions in heterogeneous photo-catalytic processes, were not produced in this system. This pioneering work represents a notable achievement in green organic synthesis under solar light energy. However, the efficiency for alcohol oxidation still requires further improvement. A similar composite was obtained by Robinson et al. [12,29,30], via combining alizarin red-sensitized ZnO or TiO₂ with AgNO₃ and TEMPO system in an aqueous solution, and the system was appealing due to the high yields in the oxidation of alcohols to their corresponding aldehydes and ketones under visible light irradiation. However, not only did this catalyst contain precious metal, but the selectivity also needs improvement. To develop an effective photocatalytic system that simultaneously enhances the activity and selectivity for alcohol oxidation under visible light irradiation, recent results have argued for the importance of smooth electron transfer in the conduction band during photocatalytic oxidation to improve the low selectivity and sluggish reaction rate [31–33]. In this regard, the presence of superior electron acceptors is significant and necessary to achieve higher efficiencies. Polyoxometalates (POMs) are an intriguing class of photocatalysts that are often compared with semiconductor materials [34,35] and can be activated by light in most similar processes. Since Jackson first reported the polyoxometalates catalyst [S₂W₁₈O₆₂]⁴⁻ for the solar light-induced photocatalytic oxidation of benzyl alcohol [36], the application of polyoxometalates has been widely studied in photocatalytic processes such as the oxidation of alcohols [37,38]. In particular, semiconductor-polyoxometalates composites have shown improved photocatalytic performance. Yoon [39] and co-workers recently reported enhanced photocatalytic reduction rates for methyl orange in a composite TiO₂-PW₁₂O₄₀³⁻ system, where PW₁₂O₄₀³⁻ played the role of electron acceptor and transmitter. Nevertheless, to the best of our knowledge, dye-sensitized TiO₂-polyoxometalates systems for the oxidation of alcohols under visible light have not been well studied thus far.

In our previous studies [40], TiO₂-(PW₁₂-TH)₈ films were successfully prepared using a layer by layer method and were applied as photocatalysts in aqueous RhB degradation. Here, in continuation of our research endeavors, we employed TiO₂-(PW₁₂-TH)₈ catalyst for the efficient and selective aerobic oxidation of alcohols under visible light. The results showed that the combined action of PW₁₂O₄₀³⁻ and TiO₂ can result in better photocatalytic performance. TH allowed for the photocatalytic application of both PW₁₂O₄₀³⁻ and TiO₂ under visible light irradiation and avoided the production of photogenerated holes in the system. In all cases, various substituted alcohols were effectively transformed to their corresponding aldehydes with almost absolute selectivity. Furthermore, the active species in the photocatalytic oxidation reaction process were explored by EPR and radical scavenging experiments. For the first time, a comprehensive mechanism for the oxidation of alcohols under visible light by the dye-sensitized TiO₂-polyoxometalates system was proposed.

2. Experimental

2.1. Sample preparation

Porous anatase TiO₂ microspheres were synthesized using the microwave-assisted method [38]. In a typical process, 0.2 mL titanium tetrachloride was dropwise added into the mixture containing ethanol (12 mL) and acetic acid (6 mL). After magnetic stirring, the clear solution was formed and then transferred into a 20 mL vial for reaction. The synthesis was performed in a 400-W microwave oven heated at 120 °C (Initiator 8 EXP, Biotage Corp). After being breacted for 15 min and cooled to the room temperature,

the TiO₂ was formed and separated by centrifugation. Finally, the resulting products were further dried under vacuum at 60 °C for use.

Preparation of the TiO₂-(PW₁₂-TH)₈ composite. Following the procedure described in our previous reported publications [40,41], the prepared porous anatase TiO₂ microspheres were immersed in poly (ethylene imine) (PEI) aqueous solution (10 mg/mL) for 30 min, and then the PEI-coated TiO₂ were immersed in a PW₁₂ (5 mM) solution and an TH solution (0.5 mM) for 30 min, respectively. After each immersion, the samples were washed with ethanol for several times. By repeating the above steps 8 times, the catalyst film TiO₂-(PW₁₂-TH)₈ was prepared. P25-(PW₁₂-TH)₈ was prepared in the same manner, but the (PW₁₂-TH)₈ composite films were adsorbed on the surface of commercially available Degussa P25.

Preparation of the SiO₂-(PW₁₂-TH)₈ composite. The SiO₂ used here was prepared according to the reported method [42]. Typically, cetylpyridinium bromide (CPB: 0.0026 mol) and urea (0.01 mol) in water (30 mL) were added to a mixture of 0.012 mol tetraethyl orthosilicate (TEOS), cyclohexane (30 mL) and pentanol (1.5 mL). Silica was formed by MW irradiation (400 W maximum power) at 120 °C for four hour. After dried in air for a day, the prepared material was further calcined in air at 550 °C for 6 h. SiO₂-(PW₁₂-TH)₈ was prepared in the same manner, but the (PW₁₂-TH)₈ composite films were adsorbed on SiO₂ surface.

Preparation of (TH)₃PW₁₂. The catalyst was prepared by a direct precipitation method from the literature [43]. In detail, 60 mL TH (0.1 mM) ethanol solution was added dropwise to the mixture of PW₁₂ solution (20 mL, 0.1 mM) and polyethylene glycol (2 mL). The mixture was stirred vigorously for 5 h. Then, the precipitates were filtered, washed with distilled water, and dried in air.

2.2. Sample characterization

Powder X-ray diffraction (PXRD) data were collected on a Rigaku MiniFlex 600 diffractometer working with Cu K α radiation. The morphology of the samples was characterized by scanning electron microscopy (SEM, JSM6700) and transmission electron microscopy (TEM, JEM2010). The optical properties of the samples were analyzed using a UV-vis spectrophotometer (Shimadzu UV-2600) and BaSO₄ was used as the background. The Brunauer-Emmett-Teller (BET) specific surface area of the samples was analyzed by nitrogen adsorption in a Micromeritics ASAP 2020 apparatus. The photoluminescence spectra of the as-fabricated catalysts films were collected by an Edinburgh FLS920 fluorescence spectrometer with an excitation wavelength at 360 nm. The photocurrent analysis was carried out in a traditional three-electrode quartz cell. Pt foils plate as the counter electrode, and Ag/AgCl as the reference electrode. The fluoride-tin oxide (FTO) glass had been thoroughly cleaned by ethanol and acetone and acted as working electrode. The catalyst (10 mg) was ultrasonicated in 0.5 mL of DMF to obtain slurry. Then, 20 μ L of the slurry was spread onto the prepared FTO glass, and the side of the glass was previously protected using scotch tape to ensure the exposed area of the working electrode was controlled at 0.25 cm². Then, the coated working electrode was dried at room temperature in air without any heating process. The electrolyte was a 0.2 M aqueous Na₂SO₄ solution without additives. The visible light irradiation source was the same light source as that used in the photoactivity tests in the following section.

The electron paramagnetic resonance (EPR) signal of the radical species was measured by a Bruker-BioSpin E500 spectrometer under room temperature. 5-Tert-Butoxycarbonyl-5-Methyl-1-Pyrroline N-oxide (BMPO) was used as spin trap. The irradiation

Download English Version:

<https://daneshyari.com/en/article/4757445>

Download Persian Version:

<https://daneshyari.com/article/4757445>

[Daneshyari.com](https://daneshyari.com)