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Research paper

Highly selective oxidation of furfuryl alcohol over monolayer titanate nanosheet under visible light irradiation

Hao Wang[a], Yujie Song[a], Jinhua Xiong[a], Jinhong Bi[a], Liuyi Li[b], Yan Yu[b], Shijing Liang[a,*], Ling Wu[a,*]

[a] *State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou University, Fuzhou, 350116, China*
[b] *Key Laboratory of Eco-Materials Advanced Technology (Fuzhou University), Fujian Province University, 350116, China*

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ABSTRACT

Monolayer $H_{1.4}Ti_{1.65}O_4{\cdot}H_2O$ nanosheet (denoted as NST) has been prepared as a photocatalyst for the oxidation of furfuryl alcohol (denoted as FA) to furaldehyde under visible light irradiation. The photocatalytic activity of NST is over 10 times higher than that of its layered counterpart. This enhanced activity may be attributed to the high percentage of exposed Lewis acid sites in NST. The in-situ FTIR result suggests that FA are efficiently chemosorbed on the exposed Lewis acid sites forming the surface coordination species via C—O groups, resulting in the activation of FA. The surface coordination species would respond to visible light absorption. Furthermore, The XAFS result shows that the signals for Ti—O and Ti–Ti in NST are weaker dramatically and the signals positions are shifted by 0.03 Å in the higher R direction as compared with those in layered counterpart, suggesting the more exposed Ti and O defects in NST. The oxygen molecules absorbed on these surface defects are activated forming $\cdot O_2^-$ by photo-electrons under visible light irradiation. Finally, a possible mechanism has been proposed at a molecular level.

1. Introduction

Aldehydes are of high industrial importance because of its use as an intermediate in the production of fine chemicals. Photocatalytic selective oxidation of alcohols to aldehydes by utilizing light energy has attracted wide attentions. They provide the possibility to using the green and renewable energy [1–3]. In the last several decades, massive photocatalysts (such as C_3N_4 [4], WO_3 [5], CdS [6] and TiO_2 [7]) have been developed for the oxidation the alcohols to obtaining the corresponding aldehydes. Up to now, the benzaldehyde, cinnamyl aldehyde, 2-thiophenecarboxaldehyde and so on have been synthesized efficiently via the selective oxidation of corresponding alcohols under the light irradiation [8–10]. However, the fact is that the furfuraldehyde, a key chemical product that widely used in synthetic plastics, pharmaceuticals, pesticides and other industries, are few studied in present photocatalytic system [11,12]. The developed catalytic system contributes to the selective oxidation of FA to furfuraldehyde. But, the low conversion of FA and the inferior furfuraldehyde selectivity lead to the materials waste and impurity product [13]. These limit their applications in general. Moreover, the elevated temperature results in the extra energy consuming [14]. Therefore, the development of the suitable photocatalysts with atom-efficiency and cost/energy savings for efficiently catalytic selective oxidation of FA to furfuraldehyde is a pressing matter of the moment.

Monolayer metal oxide nanosheet has attracted great attention due to their atomic thickness, high carrier mobility, the formation of dangling bonds and large surface area [15,16]. These unique properties endow the monolayer nanosheet the promising applications in selectivity oxidation of alcohols to aldehydes [17,18]. Analogously, the $H_{1.4}Ti_{1.65}O_4{\cdot}H_2O$ nanosheet is a lepidocrocite-type photocatalysts that consists of a polyanion layer built by a distorted TiO_6 octahedra flat and many defects. The thickness of monolayer $H_{1.4}Ti_{1.65}O_4{\cdot}H_2O$ nanosheet is only 1.2 nm. Thus, a great deal of unsaturated surface metal sites (USMSs) can be fully exposed in the monolayer nanosheet, acting as the Lewis acid sites [19,20]. In the catalytic reactions, the USMSs can interact with the FA intimately. And then, the FA molecules would be activated. This is a very important step in the oxidation of FA. Therefore, $H_{1.4}Ti_{1.65}O_4{\cdot}H_2O$ nanosheet could offer a more sustainable and environmentally friendly alternation to the traditional catalytic system for the selective oxidation of FA to furfuraldehyde. Furthermore, one of the principal issues is where and how the FA molecules bind in the surface of monolayer nanosheet. In addition, the surface defective sites make the detailed understanding of FA molecules absorbed behavior very challenging.

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[*] Corresponding authors.
E-mail addresses: sjliang2011@gmail.com (S. Liang), wuling@fzu.edu.cn (L. Wu).

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Herein, we prepared the monolayer NST for photocatalytic selective oxidation of FA molecules to furaldehyde for the first time. The surface Lewis acid sites, defects and electron structures in NST have been thoroughly studied by X-ray absorption fine structure (XAFS) and in-situ ESR spectroscopy. Moreover, the interactions between FA molecules and these special surface sites have been fully revealed by in situ molecular spectra. Based on the exhaustive characterizations, a surface coordination species between FA and NST was proposed to explain the promoted catalytic performance. Additionally, the photoelectron-chemical measurements have been also investigated to illuminate the effects of charge transport on the photocatalytic transformation efficiency. Finally, a surface coordination species promoted photocatalytic mechanism for the oxidation of FA under visible light irradiation has been revealed at a molecular level.

2. Experimental section

2.1. Reagents and chemicals

All the reagents were analytical grade purchased from Alfa Aesar China Co., Ltd, such as hydrochloric acid (HCl, 40%), tetrabutylammonium (TBAOH) hydroxide (40 wt% solution) solution, titanium oxide (TiO_2 anatase), cesium carbonate (Cs_2CO_3, 99%), zinc oxide (ZnO), Furfuryl alcohol (98%) and 2-furaldehyde (98%).

2.2. Catalyst preparation

The preparation procedures of the catalysts have been illustrated in Fig. S1. Firstly, zinc-doped titanate $Cs_xTi_{2-x/2}Zn_{x/2}O_4$ (x = 0.7) was prepared by a high temperature solid state reaction method [21]. A mixture of Cs_2CO_3, ZnO, and TiO_2 with a molar ration of 1:1:4.7 was placed in an alumina crucible. Then, the mixture was heated in air at 800 °C for 2 h, followed by calcined at 1000 °C for 20 h. The obtained sample ($Cs_{0.7}Ti_{1.65}Zn_{0.35}O_4$) was denoted as SSR. The layered $H_{1.4}Ti_{1.65}O_4 \cdot H_2O$ (denoted as LAT) was prepared by a protonic exchange. For a typical reaction, SSR was stirred in a 1 M HCl solution at room temperature for 5 days. The acidic solution was renewed every day to promote a complete ionic exchange. After the protonic exchange reaction, intercalation of organic amines was processed by dispersing 4 g of LAT into 1000 mL of TBAOH aqueous solutions with vigorously shaking for more than 5 days at the ambient temperature. The resulting colloidal suspensions were dealt with 1 M HCl solution. The obtained solid product was separated from the suspension by centrifugation. The sample was washed by deionized water. The final sample was dried in an oven at 60 °C overnight denoted as NST.

2.3. Catalyst characterization

Structural analysis of the synthetic samples was carried out by powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer operated at 40 kV and 40 mA with Ni-filtered Cu Kirradiation ($\lambda = 1.5406$ Å). UV–vis diffuse reflectance spectra (UV–vis DRS) were recorded by using a UV–vis spectrophotometer (Varian Cary 500) in which $BaSO_4$ powder was used as a reference. The data were converted to Kubelka-Munk (KM) functions. Nitrogen adsorption−desorption isotherms were measured on an ASAP 2020 M apparatus (Micromeritics Instrument Corp., USA). The sample was degassed in vacuum at 120 °C for 6 h and then analyzed at −196 °C. The morphologies and structures of the samples were examined by scanning electron microscopy (FEI Nova NANO-SEM 230 spectrophotometer). The transmission electron microscopy (TEM) and the high resolution transmission electron microscopy (HRTEM) analysis were taken by FEI model Tecnai G2 F20 S-TWIN instrument. Atomic force microscope (AFM) images were collected on a Nanoscope E multimode. The NST colloid was diluted for preparation of AFM measurement. 4ul of the suspension was dispersed on the mica plate. After air drying naturally, the sample was used to measure the thickness of the NST. X-ray photoelectron spectroscopy (XPS) measurements were carried out by using a PHI Quantum 2000 XPS system with a monochromatic Al K_α source and a charge neutralizer. All of the binding energies were calibrated by the C1 s peak at 284.6 eV. The electron spin resonance (ESR) signals were recorded with a Bruker A300 spectrometer at room temperature using a 300 W Xe lamp (Beijing Trustech, PLS-SXE300c) as light source. ^1H nuclear magnetic resonance (NMR) spectra were measured at room temperature using a Bruker MSL400 spectrometer. Fourier transform infrared (FT-IR) data were recorded for samples prepared via the standard KBr technique on a PerkinElmer Spectrum 2000 FT-IR spectrometer. The in-situ infrared spectra of pyridine adsorbed on the catalysts were obtained at a resolution of 4 cm^{-1}. A total of 64 scans were performed to obtain each spectrum. Firstly, the powder samples were first pressed into a self-supporting IR disk (18 mm diameter, 10 mg), then the disk was placed into the sample holder which could be moved vertically along the cell's tube by a magnet. Before initiating the FTIR measurements, the disk was treated under dynamic vacuum (6×10^{-4} Torr) at 150 °C for 3 h to remove surface contaminants. After the disk cooling to RT, 10 μL of pyridine was spiked into the cell with a syringe via the septum. After the adsorption-desorption equilibrium, the FTIR spectra of the sample were collected. The physisorbed furfuryl alcohol and pyridine were removed by a further evacuation at 150 °C for 3 min under 6×10^{-4} Torr, and then, another FTIR spectrum of the sample was then taken. The X-ray absorption fine structure data on the Ti K-edge of the sample were recorded at room temperature in transmission mode using ion chambers at beam line BL14W of the Shanghai Synchrotron Radiation Facility (SSRF), China. The station was operated with a Si (111) double crystal monochromator. During the measurement, the synchrotron was operated at energy of 3.5 GeV and a current between 150 and 210 mA. The photon energy was calibrated with the first inflection point of Ti K-edge of Ti metal foil.

2.4. Electrochemistry measurement

The working electrode was prepared on fluorine-doped tin oxide (FTO) glass, which was cleaned by sonicating in water for 30 min. The FTO slide was dip coated with 10 μL of slurry. The slurry was obtained from mixture of 5 mg powder and 0.5 mL pure water with sonicating for 2 h. After air drying naturally, a copper wire was connected to the side part of the FTO glass using a conductive tape. The uncoated parts of the electrode were isolated with an epoxy resin and the exposed area of the electrode was 0.25 cm^2. The electrochemical measurements were performed in a conventional three electrode cell, using a Pt plate and a saturated Ag/AgCl electrode as counter electrode and reference electrode, respectively. The working electrode was immersed in a 0.2 M Na_2SO_4 aqueous solution without any additive for 30 s before measurement. The electrochemical impedance spectroscopy (EIS) was performed at a Zahner electrochemical workstation. The photocurrent measurements were conducted on a Precision PARC workstation. The Mott-Schottky plots were obtained at three different frequencies (0.5 k, 1 k and 1.5 kHz).

2.5. Temperature-programmed desorption of ammonia measurement

The temperature-programmed desorption of ammonia was carried out on a Micromeritics Auto Chem 2920 instrument. About 50 mg of a sample was first pretreated at 180 °C for 1 h in a quartz tube, then the sample was cooled to 50 °C to allow for the adsorption of ammonium (3.0% NH_3 in N_2, 30 mL/min) for 1 h. The desorption of ammonium was conducted from 50 to 300 °C at a heating rate of 10 °C/min in a helium flow (40 mL/min), and the desorption amount was monitored by a thermal conductivity detector (TCD).