Journal of Catalysis 345 (2017) 96–103

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

To boost photocatalytic activity in selective oxidation of alcohols on ultrathin Bi_2MoO_6 nanoplates with Pt nanoparticles as cocatalyst

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ARTICLE INFO

Article history:
Received 29 September 2016
Revised 12 November 2016
Accepted 15 November 2016
Available online 8 December 2016

Keywords:
Visible light photocatalysis
Ultrathin Bi_2MoO_6 nanoplates
Selective oxidation
Benzyl alcohol
Pt nanoparticles
Superoxide radicals

ABSTRACT

Photocatalytic oxidation reactions provide a promising strategy for green synthesis of fine chemicals. However, the low photocatalytic efficiency and selectivity are the main obstacles. Herein, we report the ultrathin Bi_2MoO_6 nanoplates with thickness of ~17 nm which exhibit a superior performance in alcohol oxidation to corresponding aldehyde using O_2 under visible light irradiation, achieving *ca.* 29 times enhancement of activity compared with Bi_2MoO_6 synthesized from traditional hydrothermal method (thickness of ~250 nm). When Pt nanoparticles as cocatalyst are loaded on the surface of the ultrathin Bi_2MoO_6 nanoplates, the photocatalytic performance is further enhanced. The remarkable enhancement of activity is attributed to the ultrathin 2D geometry of Bi_2MoO_6 nanoplates, promoting the charge-separation efficiency and affording abundant catalytically active sites. The excellent selectivity of photocatalytic oxidation of benzyl alcohol on the ultrathin Bi_2MoO_6 is attributed to the different adsorption behaviors of benzyl alcohol and benzaldehyde. This study could also provide an efficient strategy for improving the photocatalytic performance by rational fabrication of two-dimensional semiconductor materials for organic synthesis.

1. Introduction

The selective oxidation of alcohols to carbonyl compounds is one of the most significant transformations in organic synthesis [1–3]. Traditionally, the selective oxidation of alcohols is achieved by hazardous, toxic stoichiometric oxidants under stringent conditions such as high temperature or pressure [1–3]. Therefore, it is imperative to develop a clean catalytic process for oxidation of alcohols using an environmentally friendly energy source and green, atom efficient oxidants such as oxygen [1,3]. Photocatalytic oxidation reaction with benign oxidants, such as O_2, is an attractive green technology and promising route for the synthesis of fine chemicals [4–8]. TiO_2-based photocatalysts have been intensively investigated for the selective oxidation of alcohols [7,8]. For instance, the pristine rutile phase of TiO_2 was demonstrated to be an efficient photocatalyst for oxidation of alcohols, but selectivity remained a major obstacle especially at high conversion, as the serious overoxidation of product was unavoidable [9]. Much endeavor has been devoted to improving the present TiO_2-based photocatalysts, exploring surface complex-TiO_2 [10,11], dye-sensitized TiO_2 [12], and metal [13] or nitrogen-doped [14] TiO_2 photocatalysts. On the other hand, nitride- and sulfide-based photocatalysts with mild oxidation ability have been developed to implement this reaction, including C_3N_4 [15], CdS [16], In_2S_3 [17], and $ZnInS_4$ [18] etc. However, most of the current photocatalysts show low activity [9–14], photocorrosion [16–18], toxicity [16] and severe conditions [15]. The challenge of selectivity together with high efficiency remains to be addressed.

Among oxide-based semiconductors, Bi_2MoO_6, naturally abundant and non-toxic, has emerged as a promising candidate [19–22]. Furthermore, Bi_2MoO_6 endows an unique layered structure which is constructed by alternate stacking of corner-shared and distorted MoO_6 octahedral slabs, and bismuth oxide $[Bi_2O_2]^{2+}$ layers [22]. Importantly, Bi_2MoO_6 has suitable valence band and conduction band positions capable of both oxygen reduction and alcohol oxidation [19]. In spite of these advantages, there is no report on selective oxidation of alcohols using Bi_2MoO_6 as a

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http://dx.doi.org/10.1016/j.jcat.2016.11.023
0021-9517/

photocatalyst so far. However, Bi_2MoO_6 as a photocatalyst suffers from low efficiency in the degradation of the contaminants [20,21] and water oxidation [19,22], which is attributed to its inherently serious charge-recombination and low surface areas. Therefore, fabricating Bi_2MoO_6 photocatalyst with abundant active sites and increased conductivity is highly desirable.

Herein, to resolve these problems, Bi_2MoO_6 nanoplates with controllable thickness are fabricated via a facile, template-free solvothermal method. Specially, the ultrathin Bi_2MoO_6 nanoplates with thickness of $\sim$17 nm exhibit a superior performance in alcohol oxidation using O_2 under visible light irradiation, achieving *ca.* 29 times enhancement of activity compared with Bi_2MoO_6 synthesized from traditional hydrothermal method (thickness of $\sim$250 nm). The remarkable enhancement of activity is attributed to the ultrathin 2D geometry of Bi_2MoO_6 nanoplates, promoting the charge-separation efficiency and affording abundant catalytically active sites. Furthermore, Pt nanoparticles are loaded as cocatalyst, and the photocatalytic performance is further enhanced. Interestingly, the ultrathin Bi_2MoO_6 nanoplates loaded with Pt nanoparticles deliver selectivity up to 95% even at conversion as high as 87%. A mechanism for the selective oxidation of alcohols on Pt/Bi_2MoO_6 nanoplates is proposed.

2. Experimental sections

2.1. Materials

Ammonium hydroxide ($NH_3{\cdot}H_2O$), glycerol, glycol, and ammonium molybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$) was purchased from Tianjin Bodi Chemical Co., Ltd. (Tianjin, China). Benzyl alcohol was supplied from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 2-methoxybenzyl alcohol, 4-methoxybenzyl alcohol, 4-methylbenzyl alcohol, 4-chlorobenzyl alcohol, *n*-octanol, D,L-1-phenethyl alcohol, and cyclohexanol were obtained from Aladdin Industrial Corporation (Shanghai, China). 4-Fluorobenzyl alcohol, 2-pyridinemethanol, and 2-thiophenemethanol were purchased from Alfa Aesar. 3-Methoxybenzyl alcohol, furfural alcohol, and 5-hydromethylfurfural were obtained from J&K Scientific. Cinnamyl alcohol was supplied from Acros Organics. Tetrabutylammonium perchlorate was purchased from Energy Chemical. All chemicals were used without further purification. Deionized water used in the synthesis was from local sources.

2.2. Preparation of photocatalysts

$Bi(NO_3)_3{\cdot}5H_2O$ (5.0 mmol) and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (0.36 mmol) were dissolved in 60 mL different solvents including water, glycol and glycerol (at 50 °C), respectively [23]. Under stirring, pH value was adjusted to 9 by using 5% NH_3 (aq.). After stirring for 0.5 h, the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 140 °C (240 °C for water) for 24 h in an oven. The products were collected by centrifugation at 10,000 rpm and washed with deionized water and absolute ethanol several times. The yellow powders were dried at 80 °C in air. Finally, the as-prepared samples that were synthesized in the solvents of glycol and glycerol were calcined at 400 °C for 2 h to remove the organic residues adsorbed on the surface.

The metal-loaded samples were synthesized by photodeposition method. Bi_2MoO_6 samples were dispersed in methanol aqueous solution (50 vol%) containing chloroplatinic acid under vacuum conditions. The mixture was illuminated by a 300 W Xe lamp (PLS-SXE 300, Beijing Perfectlight Co., Ltd.) for 2 h with magnetic stirring in a water bath continuously keeping at 283 K, and then formed Pt-loaded Bi_2MoO_6. Other metals were deposited on Bi_2MoO_6 using the same method.

2.3. Characterization

Crystal structures of the samples were collected on a powder X-ray diffraction (XRD) instrument Rigaku D/Max-2500/PC using Cu Kα radiation. Optical properties were measured by an UV–vis spectrophotometer (JASCO-V550) with $BaSO_4$ as a reference. Morphologies of the samples were examined with a (Tecnai G^2 Spirit (FEI)) transmission electron microscopy (TEM) operated at an accelerating voltage of 120 kV, a (FEI Quanta 200F) scanning electron microscopy (SEM), and a (Tecnai G^2 F30 S-Twin) high revolution transmission electron microscopy (HRTEM). BET surface areas were determined by nitrogen adsorption in a Micromeritics ASAP 2000 apparatus. The KPFM and AFM images were taken with a Bruker Dimension V SPM system equipped Pt/Ir coated tips (resonant frequency 60–100 kHz). KPFM was based on amplitude-modulation atomic force microscopy (AM-KPFM) and simultaneously provided the topography and contact potential difference (CPD) of samples. CPD images were acquired at scan rates of 0.5 Hz and tip lift height was 60 nm at tapping mode. The contact potential difference (CPD) was defined as the difference between work function of the tip and the sample. The CPD of each sample was measured with same tip in the dark and light illumination. The sample was irradiated with 450 nm laser light (40 mW cm^{-2}) for 2 min during KPFM scanning process.

2.4. Evaluation of photocatalytic activity

10 mg catalyst was suspended in 1.5 mL benzotrifluoride (BTF) solvent containing alcohol (0.1 mmol). The choice of BTF solvent was because it is inert to oxidation and has superior oxygen solubility [24]. The catalyst was blended evenly in the solution with magnetic stirring for 30 min before illumination. Reaction temperature was kept at 20 °C with a water-cooling system. The reaction solution was illuminated by a 300 W Xe lamp with a UV-cutoff filter where a majority of the light of wavelength shorter than 420 nm was blocked. The reaction solution was analyzed with an Agilent Gas Chromatograph (GC7890) equipped with a flame ionization detector and a β-DEX 225 capillary column using dodecane or undecane as the internal standard. The chemical structures of products were confirmed by GC-mass spectrometry (MS) (Agilent Technologies, GC6890N-MS5975).

Conversion of alcohol and selectivity of aldehyde was defined as follows:

$$\text{Conversion } (\%) = [(C_0 - C_{\text{alcohol}})/C_0] \times 100$$

$$\text{Selectivity } (\%) = [C_{\text{aldehyde}}/(C_0 - C_{\text{alcohol}})] \times 100$$

where C_0 was the initial concentration of alcohol and C_{alcohol} and C_{aldehyde} were the concentration of the substrate alcohol and the corresponding aldehyde, respectively.

The cycling experiments were carried out as follows. The oxidation of benzyl alcohol was done as above. After each run of cycling test, the nanoparticles were centrifuged, washed with water, ethanol, BTF for several times, dried (300 °C for 0.5 h), and used for the next run under identical conditions.

2.5. Electron paramagnetic resonance measurements

The oxygen reduction species in the photocatalytic reaction tripped by DMPO were probed using electron paramagnetic resonance (EPR) spectra recorded on a Bruker EPR A 200 spectrometer [25,26]. The sample containing Bi_2MoO_6-glycerol or 0.3 wt% Pt/Bi_2MoO_6-glycerol (1 g/L), DMPO (0.045 M), and benzyl alcohol (10 μL)