



Improvement of visible light photocatalytic acetaldehyde decomposition of bismuth vanadate/silica nanocomposites by cocatalyst loading

Naoya Murakami, Naohiro Takebe, Toshiki Tsubota, Teruhisa Ohno*

Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology, 1-1 Sensuicho, Tobata, Kitakyushu 804-8550, Japan

ARTICLE INFO

Article history:

Received 20 June 2011

Received in revised form 5 October 2011

Accepted 12 December 2011

Available online 19 December 2011

Keywords:

Visible-light responsive photocatalyst

Bismuth vanadate

Silica

Reduction cocatalyst

ABSTRACT

Photocatalytic activity of bismuth vanadate (BiVO_4) for acetaldehyde decomposition under visible light irradiation was improved by inclusion of a nanocomposition of silica as an adsorbent material and loading of platinum (Pt) or trivalent iron ion (Fe^{3+}) as reduction cocatalysts. Addition of silica enhanced photocatalytic activity due to improvement of adsorption ability, but total decomposition of acetaldehyde was not observed within 24 h of visible light irradiation. For further improvement of photocatalytic activity, BiVO_4 with an optimized amount of silica composition were modified with Pt or Fe^{3+} . Photodeposition of Pt greatly increased photocatalytic activity, and acetaldehyde was totally decomposed within 24 h of visible light irradiation.

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1. Introduction

Many studies have been conducted over the past few decades on semiconductor photocatalysts as sustainable material for environmental remediation. Titanium(IV) oxide (TiO_2) is the most appropriate material for a photocatalyst because of its excellent properties, such as its high chemical stability, nontoxicity, and high oxidation ability [1,2]. However, one drawback is that photocatalytic reaction over TiO_2 requires ultraviolet light, which hardly exists under indoor illumination conditions.

Bismuth vanadate (BiVO_4) is yellow-colored semiconductor that exhibits bandgap energy of 2.4 and 2.9 eV (monoclinic–scheelite and tetragonal–zircon structure) and has been widely used as a pigment, photoelectrochemical electrode and powdered photocatalyst [3–5]. One well-known powdered photocatalytic application for BiVO_4 is as an oxidation photocatalyst for water splitting in a Z-scheme reaction, and various kinds of BiVO_4 photocatalysts has been reported [6–10]. However, there have been only a few studies on photocatalytic decomposition of an organic compound by using BiVO_4 , and dye decomposition reaction was used in most of those studies to evaluate photocatalytic activity [11–13].

The most decisive reason is that one-electron reduction of oxygen (O_2), which is a counterpart reaction of the oxidation of an organic compound by BiVO_4 , is difficult due to its inferior conduction band potential (−0.06 to +0.02 V vs. NHE, pH 0) [3,5,14]. Therefore, a semiconductor having a potential of the less

negative conduction band than that of one-electron O_2 reduction (e.g., $\text{O}_2 + \text{e}^- = \text{O}_2^-$ (aq), −0.284 V vs. NHE; $\text{O}_2 + \text{H}^+ + \text{e}^- = \text{HO}_2$ (aq), −0.046 V vs. NHE, pH 0) was believed to be inappropriate for photocatalytic organic decomposition. Recently, several groups have resolved the problem of O_2 reduction by using a reduction cocatalyst. In the case of tungsten(VI) oxide (WO_3), a reduction cocatalyst, e.g., platinum (Pt), palladium (Pd) or copper(II) oxide (CuO), induced multi-electron reduction of O_2 (e.g., $\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}_2$ (aq), +0.682 V vs. NHE; $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$, +1.23 V vs. NHE, pH 0), resulting in efficient oxidation of an organic compound under visible light irradiation [15–18].

Another reason for the inappropriateness of BiVO_4 for organic decomposition is the difficulty in synthesis of BiVO_4 particles with large specific surface area. Although several methods for preparing BiVO_4 have been reported, BiVO_4 with a specific surface area of only a few $\text{m}^2 \text{g}^{-1}$ is obtained in almost all cases. Therefore, adsorption ability must be improved by a method other than increasing specific surface area, e.g., by composition of adsorbent materials. In the present study, we prepared a BiVO_4 nanocomposite photocatalyst with silica and a reduction cocatalyst, which increased adsorption and O_2 reduction ability, respectively.

2. Experimental

2.1. Sample preparation

2.1.1. Mesoporous silica

Silica was prepared by a previously reported method [19]. A solution containing 162.75 cm^3 of Milli-Q water, 8.5 cm^3 of hydrochloric acid, 5.56 cm^3 of butanol and 4.5 g of Pluronic P123

* Corresponding author. Tel.: +81 93 884 3318; fax: +81 93 884 3318.
E-mail address: tohno@che.kyutech.ac.jp (T. Ohno).

(EO20PO70EO20, $M_w = 5800$, Aldrich) was stirred for 1 h at 35 °C. Then 10.36 cm³ of tetraethoxysilane was added to the solution. After stirring for 24 h at 35 °C, the solution was transferred into a Teflon bottle, and then the bottle sealed with a stainless jacket was heated at 100 °C for 24 h in an oven. After the hydrothermal treatment, the residue in the Teflon bottle was dried for 24 h at 100 °C and calcined for 3 h at 550 °C.

2.1.2. BiVO₄ with and without silica composition

BiVO₄ with silica composition was prepared by a previously reported method [13]. Three mmol of Bi(NO₃)₃·5H₂O and 3 mmol of NH₄VO₃ were added to 60 cm³ of ethanol solution containing 3.0 cm³ of nitric acid (69 wt%) under stirring. For BiVO₄ with silica composition, different percentages of the prepared silica were introduced into the solution, and then the mixture was sonicated for 100 min. The samples dried by heating for 24 h at 50 °C were calcined for 3 h at 400 °C, and BiVO₄ samples with and without silica composition were obtained.

2.1.3. Modification of BiVO₄ with Fe³⁺ by the impregnation method

An aqueous suspension composed of samples (0.5 g) and an aqueous solution of iron(III) nitrate (Fe(NO₃)₃) (30 cm³) was stirred for 24 h. After stirring, the supernatant and residue were separated by filtration, and the residue was washed with deionized water several times until the ionic conductivity of the supernatant was <10 μS cm⁻² in order to remove NO₃⁻ ions, and then the particles were dried under reduced pressure.

2.1.4. Loading of Pt by the photodeposition method

An aqueous suspension composed of particles and an aqueous ethanol solution (20 vol%) containing the corresponding amount of hexachloroplatinic acid (H₂PtCl₆·6H₂O) was photoirradiated with a light-emitting diode (LED; Lumileds, Luxeon LXHL-NRR8), which emitted light at a wavelength of ca. 455 nm with an intensity of 10 mW cm⁻², under a nitrogen atmosphere with vigorous magnetic stirring for 24 h. After irradiation, photodeposited samples were obtained by washing with water several times and drying.

2.2. Characterization

Crystal structures of the particles were confirmed by using an X-ray diffractometer (Rigaku, MiniFlex II) with Cu Kα radiation ($\lambda = 1.5405 \text{ \AA}$). The specific surface areas (S_{BET}) of the particles were measured by nitrogen adsorption on the basis of the Brunauer–Emmett–Teller equation with a surface area analyzer (Quantachrome, Nova 4200e). The morphology of prepared particles was observed by scanning electron microscopy (SEM; JEOL, JSM-6701FONO) with energy dispersive X-ray spectroscopy (EDX; JEOL, JED-2300FONO).

2.3. Photocatalytic decomposition over acetaldehyde

Photocatalytic activities of samples were evaluated by photocatalytic decomposition of acetaldehyde. One hundred milligrams of powder, which has complete extinction of incident radiation, was spread on a glass dish, and the glass dish was placed in a 125 cm³ Tedlar bag (Polyvinyl fluoride, AS ONE Co. Ltd.), and the Tedlar bag was sealed by laminating after the placement of the glass dish. Five hundred parts per million by volume of gaseous acetaldehyde was injected into the Tedlar bag, and photoirradiation was performed at room temperature after the acetaldehyde had reached an adsorption equilibrium (after 2 h). In order to estimate dark adsorption ability of the photocatalysts, concentration of acetaldehyde under an adsorption equilibrium in dark was measured. The gaseous composition in the Tedlar bag was 79% N₂, 21%

O₂, <0.1 ppmv of CO₂ and 500 ppmv of acetaldehyde, and relative humidity was ca. 30%. A 500-W xenon lamp (Ushio, SX-UI501XQ) was used as a light source and the wavelength of photoirradiation was controlled by L-42 filters ($\lambda > \text{ca. } 400 \text{ nm}$, Asahi Techno Glass Co.), and an intensity of 120 mW cm⁻² was used as the light source. The concentrations of acetaldehyde and carbon dioxide (CO₂) were estimated by gas chromatography (Shimadzu, GC-8A, FID detector) with a PEG-20 M 20% Celite 545 packed glass column and by gas chromatography (Shimadzu, GC-8A, FID detector) with a Porapak N packed column and a methanizer (GL Sciences, MT-221), respectively. Five hundred microliters of gas in the Tedlar bag was injected into the chromatograph with a gas tight syringe. In the photocatalytic evaluation, a commercial BiVO₄ photocatalyst (Alfa Aesar Co., $S_{\text{BET}} < 1 \text{ m}^2 \text{ g}^{-1}$) and commercial TiO₂, P-25 (Japan Aerosil Co., $S_{\text{BET}} = 50 \text{ m}^2 \text{ g}^{-1}$), were employed as standard photocatalysts.

3. Results and discussion

3.1. Characterization of prepared samples

Fig. 1 shows XRD patterns of BiVO₄ samples with and without silica composition. Crystal structure of all BiVO₄ samples with silica composition was attributed to monoclinic–scheelite structure and an appreciable difference depending silica content was not observed. On the other hand, BiVO₄ without silica composition contained a trace amount of tetragonal–scheelite structure. Photocatalytic activity of BiVO₄ depending on crystal structure (monoclinic–scheelite, tetragonal–scheelite and tetragonal–zircon structure) has been studied, and it has been revealed that a monoclinic–scheelite structure showed higher photocatalytic activity for water oxidation under Z-scheme reaction and sacrificial electron reagent conditions [7]. Therefore, a monoclinic–scheelite structure is thought to be the most appropriate structure for photocatalytic reaction.

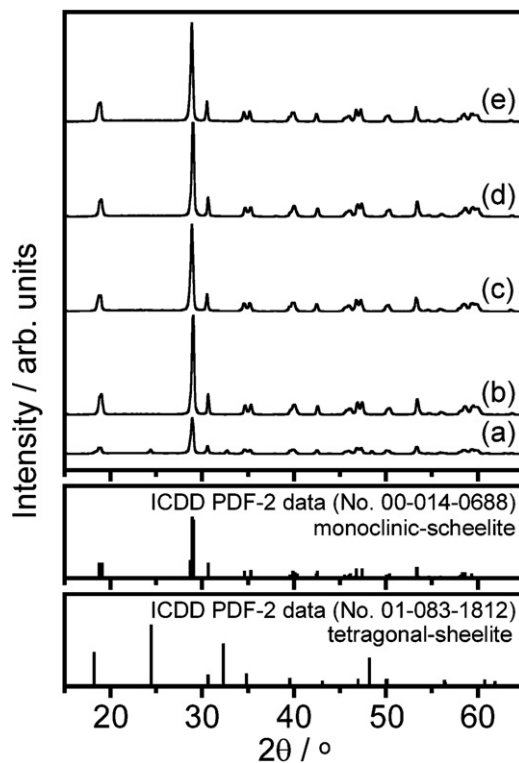


Fig. 1. XRD patterns of BiVO₄ without (a) and with (b) 2 wt%, (c) 5 wt%, (d) 7.5 wt% and (e) 10 wt% of silica composition.

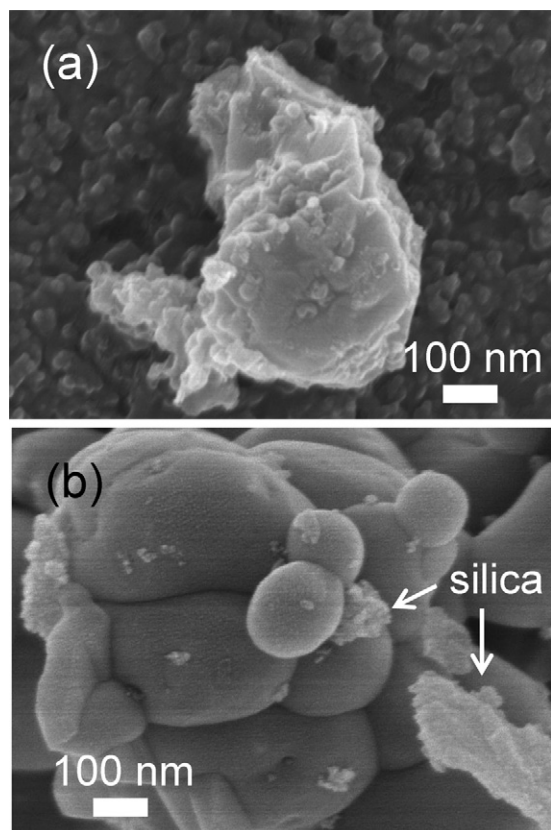


Fig. 2. SEM images of (a) silica and (b) BiVO₄ with 5 wt% of silica composition.

Fig. 2 shows SEM images of BiVO₄ samples with and without silica composition. SEM-EDX analysis indicates that large spherical particles with particle size of 100–1000 nm were attributed to BiVO₄ and that smaller particles of silica were in close contact on the BiVO₄ surface. Similar results for composite structure were obtained regardless of silica content. Specific surface area greatly increased with an increase in the amount of silica (Table 1). These results indicate that increase in specific surface area was attributed not to change in BiVO₄ but to increase in the amount of silica. This is reasonable since the specific surface area of prepared silica was 700 m² g⁻¹, which was much larger than that of BiVO₄ without silica composition (2 m² g⁻¹). On the other hand, the specific surface area of BiVO₄ with silica composition from results of the experiment was smaller than the value from calculation (Table 1). This suggests that pores of silica were filled with BiVO₄ and thus the specific surface area of BiVO₄ with silica composite decreased. Therefore, large spherical particles with particle size of

Table 1

Dependence of silica addition on specific surface area of BiVO₄ with silica composite estimated from results of the experiment (S_{BET}) and calculation (S_{cal}) and concentration of acetaldehyde under adsorption equilibrium (ACh_{eq}).

W_{ms} (wt%)	0	2	5	7.5	10	100
V_{ms}^{a} (vol%)	0	20	40	50	58	100
S_{BET} (m ² g ⁻¹)	2	10	22	31	48	700
$S_{\text{cal}}^{\text{b}}$ (m ² g ⁻¹)		16	37	54	72	
ACh_{eq} (ppmv)	419	104	160	89	104	0

^a Volume percent of mesoporous silica (V_{ms}) was calculated by using weight percent of mesoporous silica (W_{ms}), a pore volume (V_{p}) of 1.33 cm³ g⁻¹ for mesoporous silica KIT-6 [13], and densities (d_{B} and d_{S}) of 6.95 and 2.2 g cm⁻³ for BiVO₄ and silica. Here, density for mesoporous (d_{ms}) silica can be calculated as follows: $d_{\text{ms}} = 1/(V_{\text{p}} + 1/d_{\text{S}})$ [13]. Therefore, $V_{\text{ms}} = 100 (W_{\text{ms}}/d_{\text{ms}}) / [W_{\text{ms}}/d_{\text{ms}} + (100 - W_{\text{ms}})/d_{\text{B}}]$.

^b S_{cal} can be calculated as follows: $S_{\text{cal}}(W_{\text{ms}}) = S_{\text{BET}}(W_{\text{ms}} = 0) + [S_{\text{BET}}(W_{\text{ms}} = 100) - S_{\text{BET}}(W_{\text{ms}} = 0)] W_{\text{ms}}/100$.

100–1000 nm observed in SEM images were presumably formed from BiVO₄ precursor which existed outside pore of mesoporous silica before calcination.

3.2. Photocatalytic activities of BiVO₄ samples with and without silica composition

Fig. 3 shows results of photocatalytic evaluation of BiVO₄ samples with and without silica composition under visible light irradiation. Prepared BiVO₄ without silica composition showed higher photocatalytic activity than that of commercial BiVO₄ because of its larger specific surface area, but the activity was not sufficiently high. Photocatalytic reaction was increased by silica composition because adsorption ability was improved by a large increase in specific surface area. Concentration of acetaldehyde under an adsorption equilibrium in dark was decreased with increase of silica content, indicating that the silica assisted adsorption of acetaldehyde and improved photocatalytic activity (Table 1).

However, an excess amount of silica decreased photocatalytic activity. This might be due to an insufficient amount of BiVO₄ photocatalyst. For instance, BiVO₄ with 5 wt% silica composition contains 40 vol% silica and 60 vol% BiVO₄ (Table 1). Thus, an excess amount of silica decreased photoabsorption and redox sites as a result of decrease in BiVO₄ photocatalyst. Another possible reason for the decrease in photocatalytic activity is that it is difficult for acetaldehyde strongly adsorbed on the silica surface to diffuse to the surface of BiVO₄ and there was thus little oxidation of acetaldehyde on BiVO₄.

Although BiVO₄ with 5 wt% silica greatly improved photocatalytic activity, CO₂ evolution was almost stopped before 500 ppmv of CO₂ evolution. This is presumably attributed to the less neg-

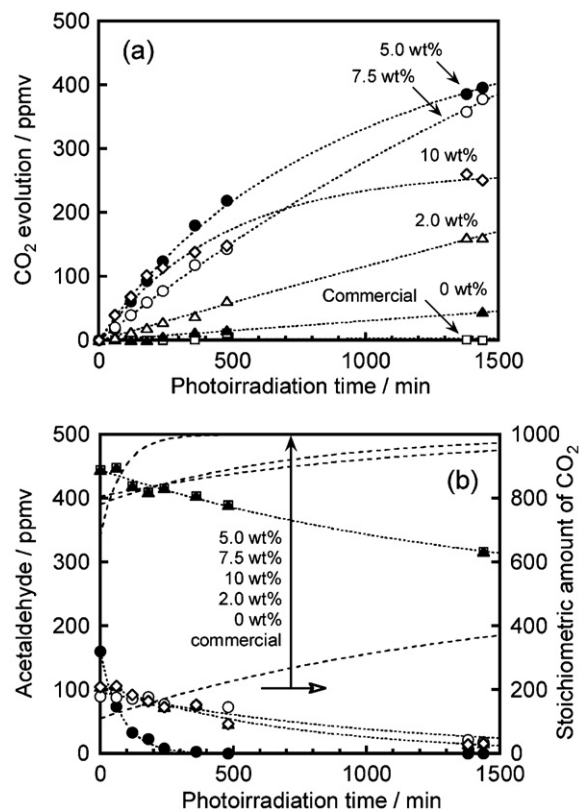


Fig. 3. Time courses of concentration of (a) CO₂ evolution and (b) acetaldehyde in gas phase over BiVO₄ with 0, 2, 5, 7.5 and 10 wt% of silica composition and commercial BiVO₄. Dashed lines in (b) shows stoichiometric amount of CO₂ calculated from decrease in acetaldehyde.

ative conduction band potential of BiVO_4 for one-electron O_2 reduction. Similar results were reported for WO_3 , and the results were attributed to its less negative potential for one-electron O_2 reduction [15–18]. WO_3 can oxidize acetaldehyde to intermediate species, i.e., acetic acid, formaldehyde and formic acid, in the initial stage of reaction, but these intermediate species are not easily decomposed and accumulate on the surface [17,18]. In the case of WO_3 , this problem was solved by using a reduction cocatalyst, e.g., Pt, Pd and CuO, which induced multi-electron reduction of O_2 [15–18]. In the present study, trivalent iron ion (Fe^{3+}) or Pt as reduction cocatalysts were loaded on BiVO_4 with an optimized amount of silica composition.

3.3. Photocatalytic activity of cocatalyst-loaded BiVO_4 with silica composition

Modification with Fe^{3+} has been reported to be effective for its utilization as a reduction cocatalyst for sulfur-doped TiO_2 [20–22]. Fe^{3+} induces efficient oxidation by accepting electrons, and generated Fe^{2+} recovers to Fe^{3+} by reacting with O_2 because BiVO_4 have a potential of the more negative conduction band (-0.06 to $+0.02$ V vs. NHE, pH 0) than redox potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ (0.771 V vs. NHE). Our group proposed that Fe^{3+} modified on TiO_2 also acts as a sensitizer for visible light [23]. However, in the present case, Fe^{3+} on BiVO_4 possibly acted as an acceptor rather than a sensitizer for visible light because the number of photogenerated electrons in BiVO_4 under the present photocatalytic conditions was much larger than that in an Fe^{3+} compound.

Fig. 4 shows results of photocatalytic evaluation of Fe^{3+} -modified BiVO_4 with silica under visible light irradiation. Photocatalytic activity was improved by Fe^{3+} modification, and more than

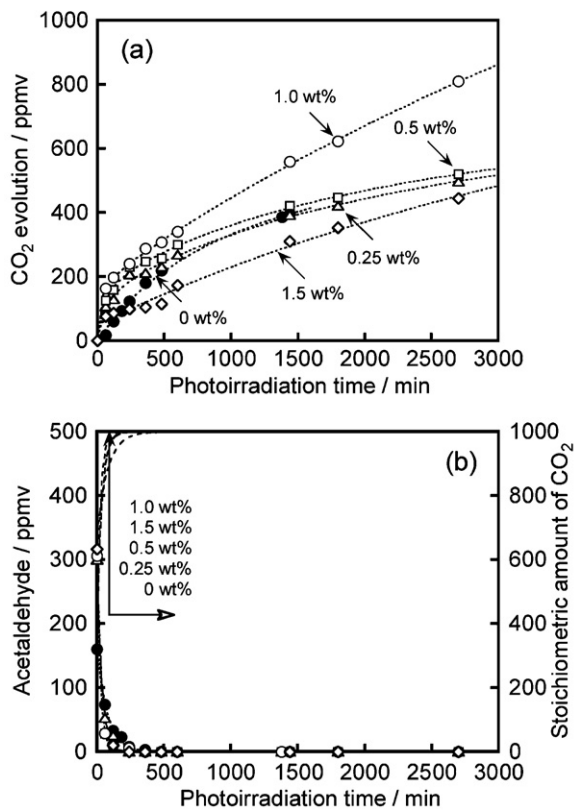


Fig. 4. Time courses of (a) CO_2 evolution and (b) acetaldehyde in gas phase over BiVO_4 /silica composite with modification of 0, 0.25, 0.5, 1.0 and 1.5 wt% Fe^{3+} . Dashed lines in (b) shows stoichiometric amount of CO_2 calculated from decrease in acetaldehyde.

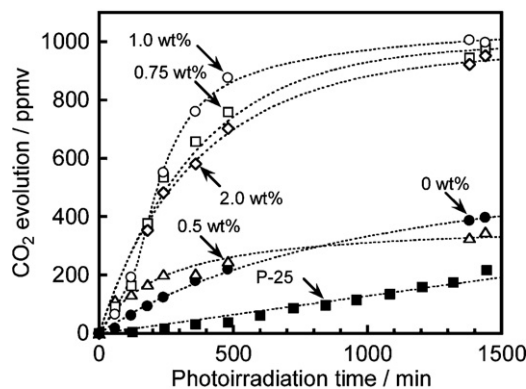


Fig. 5. Time courses of CO_2 evolution of acetaldehyde decomposition over BiVO_4 /silica composite with photodeposition of 0, 0.5, 0.75, 1.0 and 2.0 wt% of Pt, and commercial TiO_2 , P-25.

500 ppmv of CO_2 evolution was observed. This indicates that multi-electron reduction of O_2 was induced by Fe^{3+} , though a large increase in photocatalytic activity was not observed. One possible reason for this is that Fe^{3+} was adsorbed preferentially on the silica surface due to its large specific surface area. An excess amount of Fe^{3+} modification (>1.0 wt%) decreased photocatalytic activity because it is thought to intercept photoabsorption of BiVO_4 .

For preferential loading of a cocatalyst on BiVO_4 , Pt was loaded on BiVO_4 by the photodeposition method because Pt is expected to be mainly deposited on photoreduction sites (surface of BiVO_4). Pt loading on BiVO_4 possibly enhances photocatalytic activity as a result of efficient O_2 consumption by multi-electron reduction, similar to WO_3 [15–18]. Fig. 5 shows results of photocatalytic evaluation of Pt-loaded BiVO_4 with silica under visible light irradiation. Acetaldehyde in gas phase was completely disappeared in the dark because acetaldehyde was strongly adsorbed on loaded Pt. Photodeposition of Pt greatly improved photocatalytic activity, and CO_2 evolution reached 1000 ppmv, which means total decomposition of 500 ppmv of acetaldehyde. This is because Pt also induced multi-electron reduction of O_2 and efficient oxidation. However, a large amount of Pt deposition decreased photocatalytic activity because an excess amount of Pt retards photoabsorption by covering the surface. Acetaldehyde decomposition over the optimized sample was thought to be induced by direct oxidation of positive holes because the valence band potential of BiVO_4 is not positive enough ($+2.34$ to $+2.53$ V vs. NHE, pH 0) for production of OH radicals ($+2.68$ V vs. NHE, pH 0).

In order to confirm the stability, cycle test of photocatalytic activity was carried out. After few times recycles, the photocatalyst did not exhibit any significant loss of activity. Therefore, photocorrosion of the photocatalyst is thought to be less possible under our photoirradiation condition ($\lambda > 420$ nm, 120 mW cm^{-2}).

4. Conclusion

A visible light response photocatalyst for photocatalytic organic decomposition was prepared by nanocomposition of BiVO_4 , silica and reduction cocatalysts (Fe^{3+} or Pt). Addition of silica increased photocatalytic activity as a result of improvement of adsorption ability. BiVO_4 with 5 wt% of silica composition showed the highest photocatalytic activity because of an optimized balance between adsorption ability and BiVO_4 amount. Photodeposited Pt showed excellent cocatalytic performance, compared to Fe^{3+} modified by the impregnation method. This is presumably because Pt was preferentially photodeposited on the surface of BiVO_4 .

Acknowledgements

This work was supported by a grant of Knowledge Cluster Initiative implemented by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) and the New Energy and Industrial Technology Development Organization (NEDO).

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