Available online at www.sciencedirect.com
SCIENCE DIRECT
Catalysis Today 116 (2006) 18–21
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Photocatalytic properties of $CaBiVMO_8$ (where M = W and Mo) compounds

Weifeng Yao [a], Jinhua Ye [a,b,*]

[a] *Photo-Catalytic Materials Center, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan*
[b] *Precursory Research for Embryonic Science and Technology (PREST), Japan Science and Technology Agency (JST), 4-1-8 Hon-Cho Kawaguchi-shi, Saitama 332-0012, Japan*

Available online 15 May 2006

Abstract

New photocatalyts based on $CaBiVMO_8$ (where M = W and Mo) oxides were prepared by a solid-state method. The obtained $CaBiVMO_8$ powders were characterized by the XRD, UV–vis absorption spectra and BET method. The prepared $CaBiVMO_8$ materials show high photocatalytic activities for O_2 evolution and for organic compounds degradation.

Keywords: Photocatalysis; Visible light-driven photocatalysts; Scheelite structure

1. Introduction

Heterogeneous photocatalysis based on semiconductors are currently applied in various fields to solve energy problems and to clean environmental pollutions [1–5] because the photocatalysts offer great potentials for converting photon energy into chemical energy and for oxidizing organic pollutions. Recently development of highly efficient photocatalysts with visible light response has become one of the most important topics in photocatalytic research [1,3–5] because a majority of the solar spectrum is taken up by the visible light ($420 < \lambda < 750$ nm). However, despite lots of photocatalysts for water splitting or environmental pollutions cleaning under UV light irradiation have been reported, the number of visible active photocatalysts is still limited. So it is of great interest to develop new type of photocatalysts with highly photocatalytic activity.

There are some reports for scheelite structural photocatalysts, indicated the scheelite related structure is one of the interesting crystal structures for photocatalysts. $CaMoO_4$ (or $CaWO_4$) is a typical scheelite-type compound among metal molybdate (or tungstate) families with application potentials in various fields, such as in photoluminescence and microwave applications. Scheelite-type molybdates and tungstate of the divalent metal are easily soluble over the entire compositional range, which results in a rich family of solid-solution compounds [6]. From the viewpoint different from that of doping strategy, band structure engineering by making solid solutions between two compounds with different band gap has currently been regarded as one of the efficient methods for development of new photocatalysts with visible light response. These facts have motivated us to search for novel scheelite-type solid solutions photocatalysts by combining $CaMoO_4$ (or $CaWO_4$) compounds with other scheelite compounds. Scheelite $BiVO_4$, one of the active photocatayst for O_2 evolution, was selected as a candidate, because of the similar crystal structures with that of $CaMoO_4$ (or $CaWO_4$) compounds. In this paper we report a new photocatalyst $CaBiVMO_8$ (where M = W and Mo) with visible light response. Photocatalytic activity for O_2 evolution from $AgNO_3$ solutions and for methylene blue (MB) degradation with $CaBiVMO_8$ compounds as photocatalysts was examined.

2. Experimental

The $CaBiVMO_8$ (where M = W and Mo) compounds were prepared by a solid-state method. $CaCO_3$, Bi_2O_3, V_2O_5 and MoO_3 (or WO_3) were selected as starting metal source. The well-mixed powders were preheated at 600 °C for 5 h and then

* Corresponding author.
E-mail addresses: jinhua.ye@nims.go.jp, weifeng.yao@nims.go.jp (J. Ye).

0920-5861/$ – see front matter
doi:10.1016/j.cattod.2006.04.003

calcined in the temperature range 650–800 °C for 2–5 h after a vigorously reground in a mortar. The obtained $CaBiVMO_8$ powders were characterized by the X-ray diffraction (XRD), UV–vis diffuse reflectance spectrometry and the conventional Brunauer-Emmett-Teller (BET) method.

The photocatalytic O_2 evolution from an aqueous silver nitrate solution was recorded in a closed gas circulation system with a side window Pyrex cell. The light source was a 300 W Xe arc lamp attached with cutoff filters. The photocatalyst (0.5 g) was dispersed in 270 ml aqueous $AgNO_3$ (0.85 g) solution. The evolved O_2 gas was determined by a thermal conductivity detector gas chromatograph (TCD, Shimadzu GC-8A), which was connected to the system with a circulating line. The activity of WO_3 (Wako Pure Chemical Industries Ltd.) (used as received without further treatment), one of the well known heterogeneous photocatalysts with high activity for O_2 evolution, was examined for a comparison. The decolorization of methylene blue solution was carried out in a Pyrex glass cell with constant magnetic stirring. Reaction suspension was prepared by adding 0.3 g of the prepared samples into a 100 ml of aqueous MB solution. The light source was a 300 W Xe arc lamp attached with a cutoff filter and a water filter. Prior to irradiation, the suspensions were magnetically stirred in a dark condition for 30 min to establish adsorption/degradation equilibrium. The concentrations of aqueous MB solution were determined by measuring the absorbance at 656 nm with an UV–vis spectrophotometer.

3. Results and discussion

X-ray diffraction patterns of $CaBiVMO_8$ (M = W and Mo) compounds were examined. As shown in Fig. 1, the prepared powders were well crystallized when calcined at 650 °C. By profile simulation on the basis of previous works, the prepared $CaBiVMO_8$ (M = W and Mo) were mainly crystallized in tetragonal scheelite structure similar as that of scheelite $CaMoO_4$ (or $CaWO_4$), except a small mount of Bi_2O_3 impurity. The content of the impurity, which can be evaluated by comparing the peak area of the impurity with that of samples, is about 6.5 at.%. Such a small quantity of the impurity phase could not significantly modify the photophysical and photocatalytic properties of $CaBiVMO_8$ compounds. The effects of calcined temperatures on crystalline of $CaBiVMO_8$ compounds were detected. Fig. 2 shows the typical results for the $CaBiVMoO_8$ compounds. It can be seen that the intensity of the impurity peaks decrease with the increasing heat-treatment temperatures and the phase-pure $CaBiVMO_8$ compounds could be obtained when calcined at 800 °C. However, because of the easily volatilized Bi, V and Mo oxides at high temperature, the photocatalytic activities of the prepared samples were found to decrease significantly with the increasing treating temperatures. So in this paper, the $CaBiVMO_8$ prepared by pretreated at 600 °C for 5 h and then calcined at 650 °C for 2 h were selected as the model photocatalysts for the rest characterizations.

The UV–vis absorbance spectra of the $CaBiVMO_8$ compounds were measured, as shown in Fig. 3. The UV–vis absorbance spectra for $BiVO_4$, $CaWO_4$ and $CaMoO_4$ were also given for reference. It is clear that the $CaBiVMO_8$ compounds show abilities to absorb visible light. The absorption edge of the $CaBiVMO_8$ was found in a position between those of $BiVO_4$ and $CaMoO_4$ ($CaWO_4$) prepared under similar conditions. The band gaps of the $CaBiVWO_8$ and $CaBiVMoO_8$ crystals were estimated to be 2.51 and 2.41 eV, respectively, from the onsets of the absorption profile. For a comparison, the band gap of $BiVO_4$, $CaMoO_4$ and $CaWO_4$ were detected as 2.34, 3.64 and 3.8 eV, respectively. The color of the prepared $CaBiVMO_8$ compounds was vivid yellow and the surface areas of the prepared $CaBiVMoO_8$ and $CaBiVWO_8$ were 0.6 and 0.7 $m^2\ g^{-1}$, respectively.

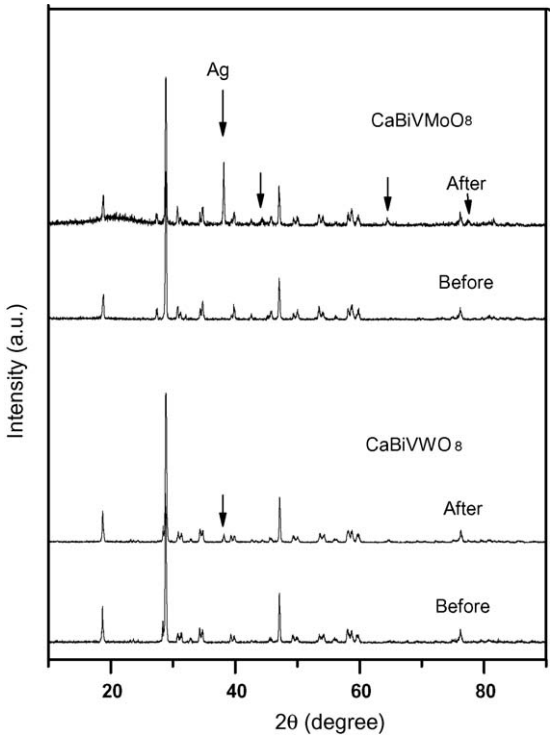

Fig. 1. XRD patterns of $CaBiVMO_8$ (M = W and Mo) solid solutions before and after the photocatalytic O_2 evolution. The arrows marks indicated the peaks of the metallic Ag.

The photocatalytic activities of O_2 evolution from the aqueous $AgNO_3$ solution with $CaBiVMO_8$ photocatalysts under visible light irradiation (>420 nm) were detected. As shown in Fig. 4, the $CaBiVMO_8$ compounds displayed high activities for O_2 evolution from $AgNO_3$ solution under visible light irradiation. However, the rate for O_2 evolution over each photocatalyst decreased with the increasing irradiation time. This result is usually observed for such photocatalytic O_2 evolution reactions, which was attributed to the photodeposition of metallic Ag on the surface of the photocatalysts particles and shielded the catalysts from the incident light. Therefore, the initial rate of the O_2 evolution was selected as the activity of the reaction. The obtained maximum activities of $CaBiVMoO_8$ and $CaBiVWO_8$ were 52.96 and 15 μmol/h, respectively. As a comparison, the activity of WO_3 and $BiVO_4$ (prepared by the solid-state) were 30.11 and 21.8 μmol/h, respectively, under the present conditions. The XRD patterns of $CaBiVMO_8$ photocatalysts were not changed after the reaction, as shown in

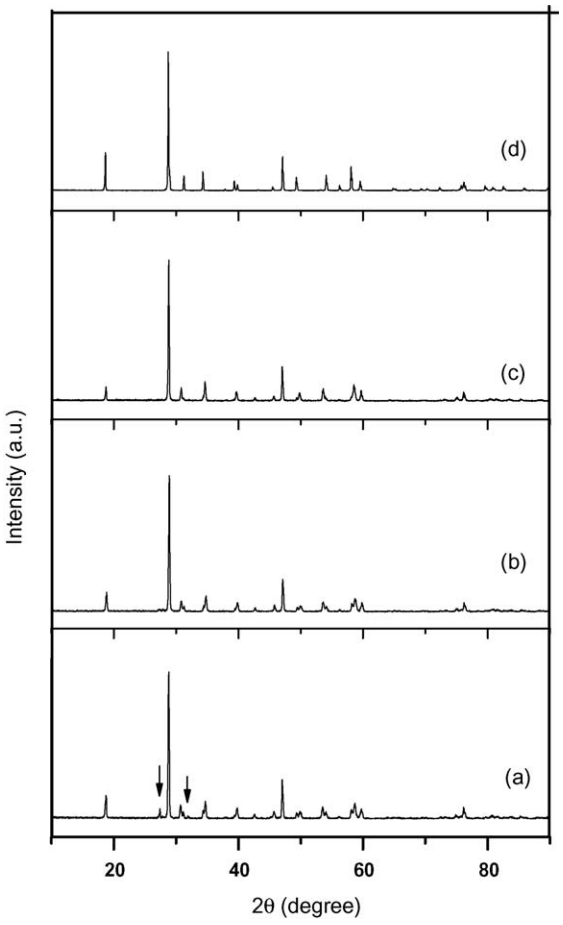

Fig. 2. Crystalline dependence of treating temperatures for $CaBiVMoO_8$ solid solutions. Preparation condition: calcined at (a) 650 °C, (b) 700 °C, and (c) 800 °C, and (d) $CaMoO_4$ calcined at 650 °C.

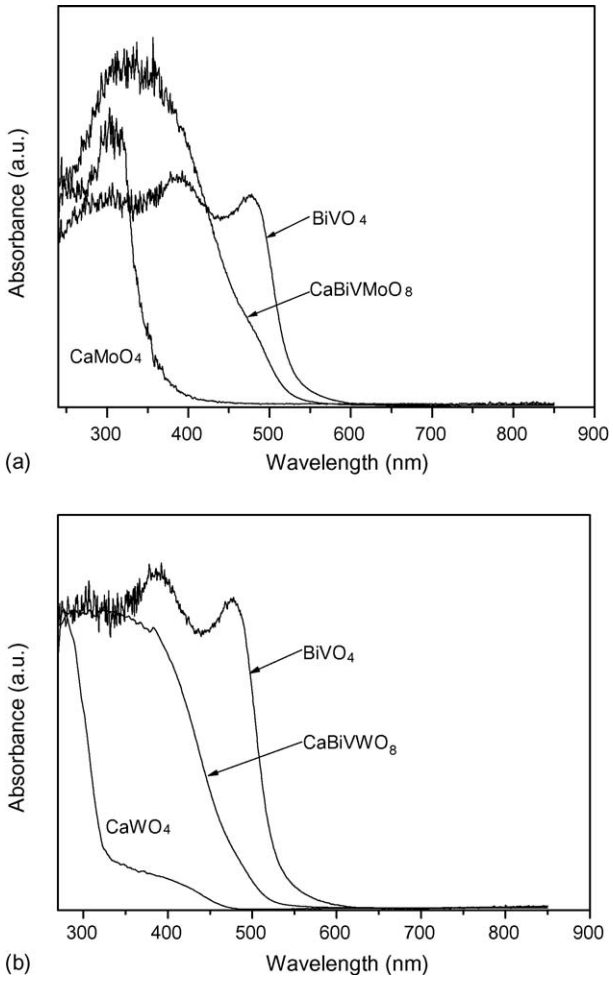

Fig. 3. Diffuse reflectance spectra of $CaBiVMO_8$ (M = W and Mo), $CaWO_4$, $CaMoO_4$ and $BiVO_4$ oxides. Preparation condition: pretreated at 600 °C for 5 h then calcined at 650 °C for 2 h.

Fig. 1, except several new metallic Ag peaks appeared, indicating the catalysts being stable during the reaction. Further experiments show the wavelength dependence of the photocatalytic activity for O_2 evolution agreed well with the UV-absorption spectra, suggesting the O_2 evolution reaction is driven by the visible light. The photocatalytic process for H_2 evolution in aqueous CH_3OH solution with Pt cocatalyst was also attempted, but no H_2 evolution was detected after 10 h light irradiation, indicating the potential of the $CaBiVMO_8$ conduction bands is not high enough for the H_2 evolution by H_2O reduction.

Photocatalytic activities of $CaBiVMO_8$ compounds for the degradation of organic pollutions are detected. One Azo dye, methylene blue (MB) was selected as a model organic material. The photocatalytic decolorization of the methylene blue aqueous solution on each photocatalysts was performed according to the procedure indicated in the experimental section. Fig. 5 shows the results of the photo-decolorization of MB solutions over $CaBiVMO_8$ compounds under visible light irradiation (>420 nm). As a comparison, MB degradation over P25 and the effect of photolysis on MB decolorization under light irradiation were also measured under the present condition. It is notable that the decrease of methylene blue over P25 catalysts was similar to that in MB photolysis process, suggesting the P25 was inactive for MB degradation under visible light irradiation. However, MB degradation on the $CaBiVMO_8$ compounds was remarkable. As shown in Fig. 5, the nearly complete degradation of the MB can be reached on

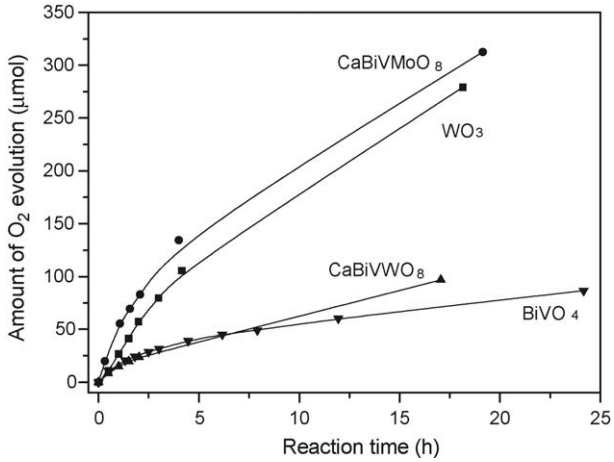

Fig. 4. Formation rates of O_2 evolution over $CaBiVMO_8$ (M = W and Mo) photocatalysts from $AgNO_3$ solution under visible light irradiation (>420 nm).

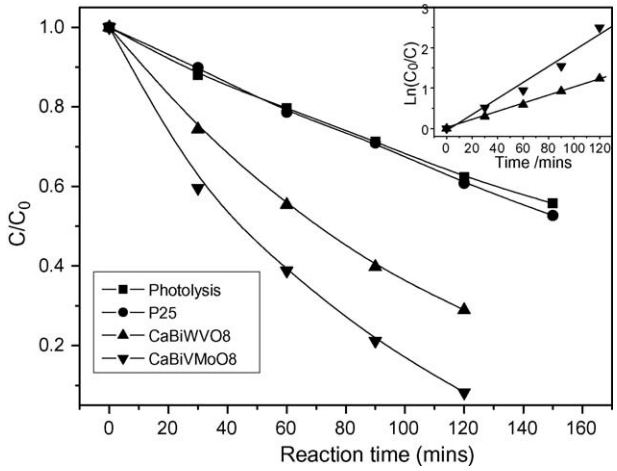

Fig. 5. Photo-decolorization of MB solutions over $CaBiVMO_8$ and P25 photocatalysts under visible light irradiation (>420 nm). Insert: the apparent first-order linear function of $\ln(C_0/C)$ vs. time for the MB degradation reaction over $CaBiVMO_8$ catalysts.

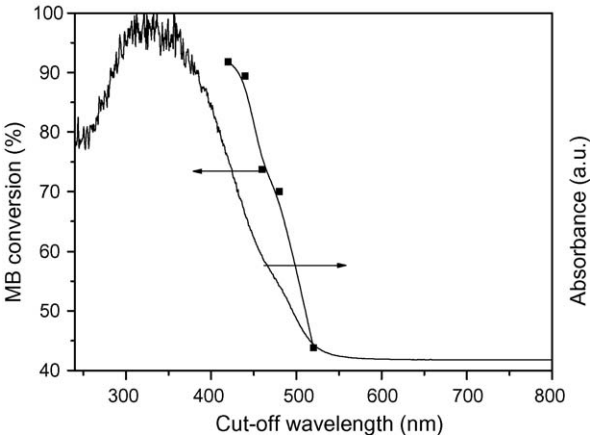

Fig. 6. Dependence of MB conversion upon cutoff wavelength of filters with $CaBiVMoO_8$ photocatalysts at room temperature in air. Catalysts: 0.3 g. Light souse: 300 W Xe lamp with cutoff filters. Reaction time: 2 h.

$CaBiVMoO_8$ photocatalysts after 2 h reaction. The photocatalytic degradation of Azo dyes generally follows a Langmuir-Hinshelwood mechanism [7–9] with the rate r being proportional to the coverage θ, which becomes proportional to C at low concentrations: $r = k\theta = k\mathrm{KC}/(1 + \mathrm{KC})$, where k is the true rate constant and K is the adsorption constant. When using a low dye concentration, the term KC in the denominator can be neglected and then the rate becomes a first-order function $r = -\frac{dc}{dt} = k\mathrm{KC} = k_{app}C$ where k_{app} is the apparent rate constant of pseudo-first-order. Assuming that Langmuir-type adsorption of MB occurred on the $CaBiVMO_8$ surface, the integral form $C = f(t)$ of the rate equation can be write as $\ln\frac{C_0}{C} = k_{app}t$, because of a low used concentration of MB (16 mg/l). As shown in Fig. 5, the apparent first-order linear transforms are given as an insert figure. It is clear to note that the first-order kinetics is observed for the degradation of MB on $CaBiVMO_8$ compounds. The slopes yield apparent rate constants of 0.02 and 0.01 min^{-1} for $CaBiVMoO_8$ and $CaBiVWO_8$, respectively.

The light wavelength dependence of photocatalytic activities of $CaBiVMO_8$ compounds is examined. A typical result for the $CaBiVMoO_8$ compounds was shown in Fig. 6. The wavelength dependence of the photocatalytic activity for Azo dye degradation on semiconductors catalysts is often used to examine if the reaction is driven by the light absorption. In the present condition, as shown in Fig. 6, it is obvious that the variation of photo-degradation rate of MB on $CaBiVMoO_8$ compounds was in good consistence with that of UV–vis absorption spectra, suggesting the reaction of MB degradation over $CaBiVMoO_8$ compounds should be driven by the visible light. In another word, the degradation of MB over $CaBiVMoO_8$ compounds prefers to be caused by a photocatalytical reaction rather than by a photoabsorption or photolysis effect. The calcinations of the MB and photomechanism of the reaction over $CaBiVMO_8$ compounds are still in progress.

In summary, the well-crystallized $CaBiVMO_8$ compounds (where M = W and Mo) can be obtained by the solid-state method. The band gaps of the $CaBiVWO_8$ and $CaBiVMoO_8$ were estimated to be 2.51 and 2.41 eV, respectively. The prepared materials show highly photocatalytic activities for O_2 evolution and for organic compounds degradation. The present results show that new photo-catalysts with visible light response can be produced by band engineering method even in scheelite structure oxides, suggesting making solid-solution is a promised way for developing new active photocatalysts.

Acknowledgment

The author would like to thank Ms. Liqun Yang for her help in the experiments, and thank the Japan Society for the Promotion of Science (JSPS) fellowship for financial support. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japanese Government.

References

[1] Z.G. Zou, J.H. Ye, K. Sayama, H. Arakawa, Nature 414 (2001) 625.
[2] D.F. Wang, Z.G. Zou, J.H. Ye, Chem. Phys. Lett. 384 (2004) 139.
[3] J.W. Tang, Z.G. Zou, J.H. Ye, Chem. Mater. 16 (9) (2004) 1644.
[4] J.W. Tang, Z.G. Zou, J.H. Ye Angew, Chem. Int. Edit. 43 (34) (2004) 4463.
[5] J. Yin, Z.G. Zou, J.H. Ye, J. Phys. Chem. B 108 (26) (2004) 8888.
[6] S.H. Yu, B. Liu, M.S. Mo, J.H. Huang, X.M. Liu, Y.T. Qian, Adv. Func. Mater. 13 (8) (2003) 639.
[7] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.-M. Hertmann, Appl. Catal. B Environ. 31 (2001) 134.
[8] J.C. Yu, J. Yu, J. Zhao, Appl. Catal. B Environ. 36 (2002) 31.
[9] W.F. Yao, X.H. Xu, H. Wang, J.T. Zhou, X.N. Yang, Y. Zhang, S.X. Shang, B.B. Huang, Appl. Catal. B Envion. 52 (2) (2004) 109–116.