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A NEW ACTIVE SULFUR-SENSITIVE BISMUTH OXIDE ON TITANIA FOR PHOTOCATALYST

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Abstract – Bismuth oxide on titania catalyst was prepared and characterized, and its photocatalytic activitiy was tested. Also investigated was the possibility of a sulfur-sensitive photocatalytic property of bismuth oxide on titania catalyst. It showed high photocatalytic activity, especially in the presence of polysulfide as one of the sacrificial agents. The activity of the evolution of hydrogen from the solution containing polysulfide showed a maximum at 5 wt% of loading of bismuth oxide on titania. The main cause of its activity, which could be explained by the amounts of sulfur and of hydroxyl ion adsorbed on bismuth oxide, was inferred from the characterization of the surface state of bismuth oxide on titania, considering the extent of exposure of bismuth on the catalyst surface which could provide adsorption sites of sulfur in solution if treated by reduction and/or oxidation.

Key words : Hydrogen Evolution, Hole Scavenger, Bismuth Oxide, Polysulfide, Photocatalyst

INTRODUCTION

Recently, intensive catalytic research on the removal of toxic materials as well as environmentally hazardous ones such as volatile organic molecules, cyanides, sulfides etc., has been performed by using a photocatalyst [Al-Sayyed et al., 1991; Childs et al., 1980; Frank et al., 1977; Pellizetti et al., 1984; Reber et al., 1984; Serpone et al., 1984., Ueno et al., 1985; White et al., 1985]. Another aim of this research was to harvest energy efficiently, as a form of hydrogen which has been known as a clean alternative energy source. However, this kind of reaction did not give high quantum yield in producing hydrogen from water splitting, and so an effort has been made to enhance the quantum yield [Domen et al., 1982; Pellizetti et al., 1984; Sato, 1988].

To solve the above problem, an endeavor to develop a new high-performance photocatalyst has been made. Recently it was reported that mixed metal oxide based on bismuth oxide could possibly give a new family of photocatalysts. In these catalysts, bismuth oxide could provide different types of properties such as band gap and structure [Harriman et al., 1988].

For another solution, an appropriate hole scavenger, for the purpose of retarding the recombination of a photogenerated electron and hole and enhancing the reactivity of a photogenerated hole, could be chosen. By now methanol has been a promising hole scavenger. However, the use of methanol should be avoided because of its potent availability of energy source itself [Kawai et al., 1979; Pichat et al., 1981]. So, several researchers have tested the photocatalytic activity of CdS in the presence of sulfide as an efficient sacrificial agent as well as an alternative choice of wastewater which needed treatment as a toxic material; it showed a high quantum yield up to about 25 % [Pellizetti et al., 1984].

In this paper, for the extension of our research, a new sulfur-active characteristic was observed in doping bismuth oxide on titania. We prepared bismuth oxide on titania with different loading, studied the surface states and the crystal structure, tested the photocatalytic activity of bismuth oxide on titania in the presence of polysulfide as a model compound of sulfur-containing ones, and finally induced the relationship between the photocatalytic activity and the properties of bismuth oxide.

EXPERIMENTAL

1. Preparation of Catalysts

For the preparation of the bismuth oxide on titania, an appropriate amount of bismuth nitrate (Hanawa, GR grade) was dissolved into a solution formed by 20 ml of HNO_3 and 180 ml of water. Then 10 g of titania (Aldrich, anatase 99.9 %+) was added into the above solution. After water was evaporated at 80 °C, the remaining particles were dried at 100 °C, overnight. The fully dried catalyst precursor was calcined at 500 °C for 4 hours. To verify the effect of the surface state of bismuth oxide on titania, we prepared various kinds of the different weight percent of bismuth oxide to titania, i.e., 2, 5, 8, 10, and 20. In the description of xB-O500 catalyst, O 500 denoted catalyst after being calcined at 500 °C for 4 hours, and the xB denoted x wt% of bismuth oxide to titania. And in xB-R400, R400 denoted the treatment of the reduction of xB-O500 catalyst at 400 °C for 1 hour, and in xB-R5O4, R 5O4 denoted the treatment of the reduction of xB-O500 catalyst at 500 °C for 1 hour followed by reoxidation at 400 °C for 1 hour.

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2. Preparation of Polysulfide-Containing Solutions

Mother liquid containing polysulfide used in the aqueous state was prepared by the following sequence: (1) 80 g of NaOH was dissolved in 2,000 ml water, (2) 6.4 g of sulfur powder was put into the solution of (1), (3) 5 ml of CS_2 was dropped into the solution of (2), (4) After being stirred for at least 24 hours, the undissolved sulfur powder in the solution of (3) was filtered, giving polysulfide in aqueous state. The concentration of sulfur in the final polysulfide-containing solution was 1.3 mg S/ml of mother liquid solution.

3. Photocatalytic Activity Test

Fig. 1 shows a schematic diagram of the photocatalytic reaction apparatus used in this study. The carrier-gas-flow type photoreactor was a Pyrex cylinder of ca. 600 ml whose inner part was jointed with a quartz cylinder as a window of lamp. Temperature was controlled by $25\pm1\,^{\circ}C$ during illumination of light. UV irradiation was carried out with a high-pressure mercury lamp (450 W, Kum-Kang Co.). The volume of solution illuminated was constantly 500 ml. In each experiment, oxygen-free N_2 was bubbled continuously at a rate of 20 ml/min throughout the illumination. For quantitative analyses of gas components of the product, 0.5 ml gas sample was analyzed by a gas chromatograph (Yanaco, G1800T). And the converted sulfur was identified by ion chromatography and mass spectrometry. For comparative analyses of quantum yield, the photon flux from the lamp was measured by a method of chemical actinometry using potassium ferrioxalate as a chemical actinometer. The measured photon flux was 3×10^{-6} einstein/sec, and this quantity of photon flux was tantamount to 4.75 mmol H_2 per hour. So, the catalytic activity in this study was defined as the rate of hydrogen evolution from water.

4. Other Instrumental Analyses

The amount of sulfur adsorbed on bismuth oxide in Bi_2O_3/TiO_2 catalyst was measured by DR-2000 as a turbidity of $BaSO_4$ colloidal formed by sulfate and $BaCl_2$. The amount of hydroxyl ion on the catalyst was measured by titration with dilute HCl. The reductive/oxidative property of bismuth oxide on titania was identified by a temperature-programmed reduction technique. The crystal structure of the prepared bismuth oxide on titania was determined by XRD (X-ray diffraction). For the identification of the band gap of the catalyst and the photo-induced property, UV-DRS (UV-diffuse reflectance spectroscopy) was used. The shape and the location of bismuth oxide on titania was visualized by SEM (scanning electron microscopy), and the composition of the catalyst was determined by EDX (energy dispersive X-ray emission spectroscopy) simultaneously. The binding states of oxygen and bismuth were measured by XPS (X-ray photoelectron spectroscopy).

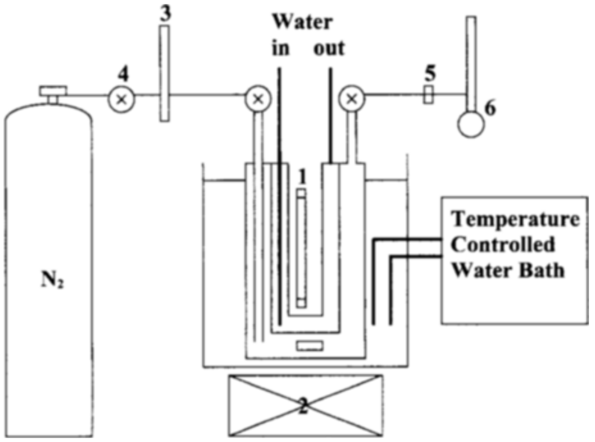

Fig. 1. Schematic diagram of photocatalytic reactor system.

1. Mercury lamp	4. Valve
2. Magnetic stirrer	5. Septum
3. Flowmeter	6. Bubble meter

RESULTS AND DISCUSSION

1. Properties of Polysulfide-Containing Solutions

Fig. 2(a) shows a representative UV-Vis spectrum of polysulfide obtained by the method in this study, and gives absorption peaks at 315, 335 and 390 nm. Their exact peak assignments have not been established yet, but we assumed them to be assigned to S_2^{2-} (peak at 335 nm) and S_3^{2-} (peaks at 315 and 390 nm) [Giggenbach, 1972; Plichon et al., 1981]. As the stirring time goes on, however, the above peaks [Fig. 2(a)], even in the absence of light, were shifted bit by bit to 310 and 370 nm of polysulfide as shown in Fig. 2(b) to (f), respectively. From the changes of peak positions, we supposed the conversion went from S_2^{2-} and S_3^{2-} as an initial state of polysulfide to S_4^{2-} and/or S_6^{2-} of more stabilized form(s).

2. Photocatalytic Activity

In the comparison of activities between 5 wt% NiO/TiO_2 and 5 wt% Bi_2O_3/TiO_2 in the presence of polysulfide as a hole scavenger, the latter exhibited 4.7 times higher activity than the former. In other metals or metal oxides such as Pt, Ni, In_2O_3, Nb_2O_3, and RuO_2, an enhanced activity could not be observed. From this result, bismuth oxide could give an

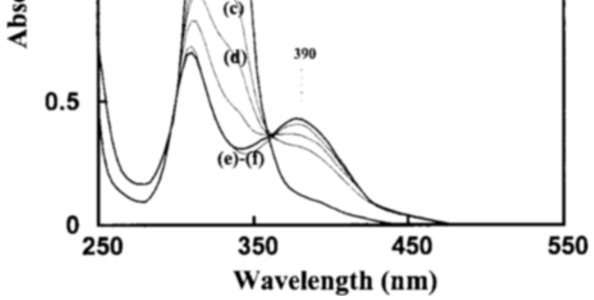

Fig. 2. UV absorbance spectra of polysulfide for various stirring periods.
(a) initial, (b) 1 hour, (c) 2 hours, (d) 3 hours, and (e)-(f) 4-5 hours

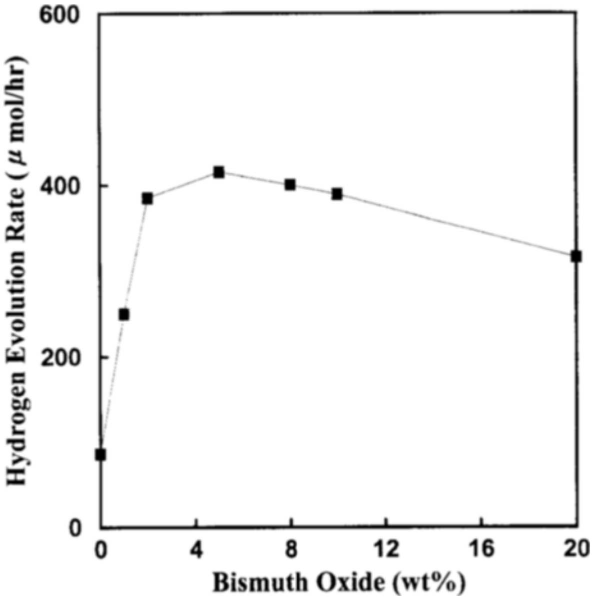

Fig. 3. Rate of hydrogen evolution on xB-O500 catalyst as a function of loading of Bi_2O_3 on TiO_2, xB.

Table 1. Rate of hydrogen evolution and amount of sulfur adsorbed on the catalysts treated with reduction and/or (Re)oxidation of 10B-O500 catalyst

Catalyst	10B-R400	10B-R5O4	10B-O500
Rate of hydrogen evolution (μmol/hr)	454	265	395
Amount of sulfur adsorbed (μmol/g-cat.)	194	156	191

outstandingly improved activity and afford an efficient photocatalyst candidate. Fig. 3 shows the photocatalytic activities (hydrogen evolution rates) of xB-O500 catalysts (x=0, 1, 2, 5, 8, 10, and 20) in the presence of polysulfide. The activity showed a maximum around 5 wt% of bismuth oxide and then decreased.

As shown in Table 1, in the comparison of activities among 10B-R400, 10B-O500, and 10B-R5O4 catalysts which were treated differently, the 10B-R400 catalyst showed the highest activity among them. The rates of hydrogen evolution over the above three catalysts were fairly correlated with the amounts of sulfur adsorbed on the catalysts. A reasonable explanation for the results will be made in the following sections.

3. The Study of TPR (Temperature-Programmed Reduction)

Fig. 4 shows the TPR profiles of xB-O500 catalysts with different loadings of bismuth oxide on titania. In low loadings of bismuth oxide below 5 wt%, only a broad reduction peak covering a wide range from 250 to 500 °C was observed, while in higher loadings two separable reduction peaks, which were assigned to a lower temperature surface oxygen (denoted as 'α-state') below 400 °C and a higher one (denoted as 'α-state') above 400 °C, were detected. The higher the loading of bismuth oxide, the stronger the intensity of the β-state peak. And its maximum peak temperature was unchanged although the loading of bismuth oxide increased.

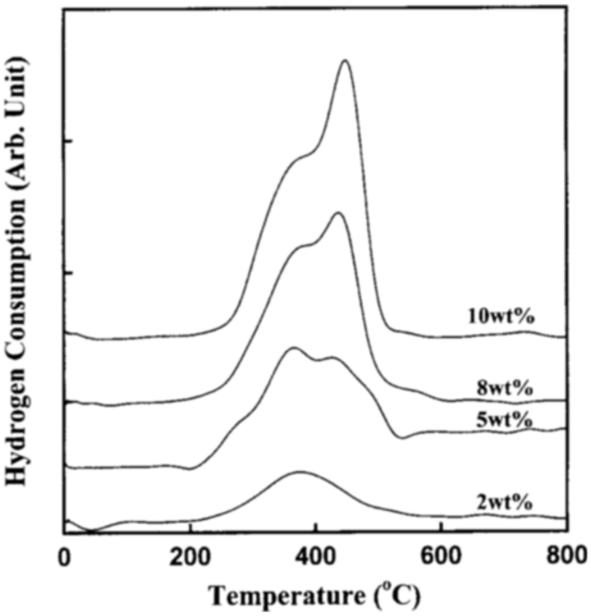

Fig. 4. TPR profiles of xB-O500 catalysts with different loadings of Bi_2O_3 on TiO_2, xB.

For clearer examination of surface oxygen species in 10B-O500 catalyst, the separation of the β-state from the whole spectrum was needed. First, to remove the α-state, the 10B-O500 catalyst was reduced at 400 °C for 1 hour giving 10B-R400. However, the state of surface oxygen species after reduction did not agree with our expectation, as shown in Fig. 5(c). The lower temperature oxygen species, α-state, still remained. Secondly, to remove the β-state, the 10B-O500 catalyst was reduced at 500 °C for 1 hour followed by reoxidation at 400 °C for 1 hour, but in this case only the β-state oxygen species appeared as shown in Fig. 5(b). Fig. 5(a) shows the TPR profile of 10B-O500 catalyst. The two peaks

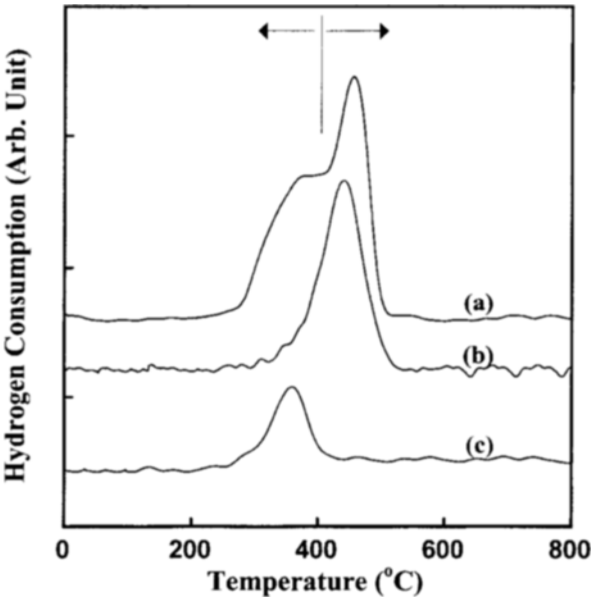

Fig. 5. TPR profiles of various 10 wt% Bi_2O_3/TiO_2 catalysts with different treatments, (a) O500, (b) R5O4, and (c) R400.

were deconvoluted to α- and β-states, and their peak areas and positions were consistent with those of 10B-R400 and 10B-R5O4 catalysts, respectively.

The 10B-R400 catalyst tinted to dark gray was considered to be partially reduced, whereas the 10B-R5O4 catalyst, partially oxidized as like. Typically in the 10B-R5O4 catalyst, the β-state was also formed even at a lower temperature of 250 °C, not at 400 °C, and even for only a shorter time of 5 minutes at 250 °C. From the above result, the formation of α-state oxygen was an activated process, and the β-state oxygen was activatedly convertible into the α-state under a reducible condition. The measurement of catalytic activity suggests that the β-state oxygen is less reactive to sulfur-containing molecule than the α-state oxygen, giving a negative effect on the activity.

The above result and the activity result (Fig. 3) suggested that the photocatalytic activity of bismuth oxide might be dependent on the amount of α-state of oxygen. The β-state of oxygen in TPR profiles increased with the loading of bismuth oxide proportionally, suggesting that this state of oxygen did not have a detrimental effect on the photocatalytic activity, but rather a negative effect. This explains the reason for the maximum activity of bismuth oxide at 5 wt% as shown in Fig. 3.

In order to obtain only α-state oxygen from the mixed oxygens of α- and β-states by an appropriate reduction and/or oxidation, the xB-O500 (x=5, 10, 15 and 20) catalysts were reduced at 400 °C for 1 hour resulting in xB-R400 catalysts, as confirmed in Fig. 5(c). And then the activity was correlated with the amount of α-state oxygen. Fig. 6 shows the photocatalytic activities of xB-R400 (x=5, 10, 15, and 20) catalysts in the presence of polysulfide. The inset shows that the area of α-state oxygen increases linearly with the increase of loading of bismuth oxide on titania. The photocatalytic activity did not increase above 5 wt% of loading of bismuth oxide as shown in Fig. 3, while the activity increased with the loading of bismuth oxide proportionally in Fig. 6 giving the same trend as that in the inset of Fig. 6. From this result, we concluded that α-state oxygen was mostly responsible for the activity.

4. The Study of XRD Measurement

Fig. 7(a) shows the XRD pattern of 10B-O500 catalyst, mainly characteristic peaks of titania in anatase form. The characteristic peaks of bismuth oxide were observed at 27.8, 30.0, and 32.9 of 2 θ value, which were correlated nicely with the peaks of α-Bi_2O_3. It is generally known that the α-Bi_2O_3 crystalline structure is easily and mainly formed by calcining at 400-450 °C for the hydroxylated product of bismuth nitrate. Fig. 7(b) shows the XRD pattern of 10B-R400 catalyst. In the case of 10B-R400 catalyst, a new diffraction pattern was observed at 27.2, 28.4, 39.7, 46.2, 48.9, and 64.6 of 2 θ value, which could be assigned to BiO. Whereas in the case of 10B-R 5O4 catalyst, as shown in Fig. 7(c), another new characteristic diffraction pattern of bismuth oxide was observed at 28.0, 31.7, 32.7, 46.2, 47.0, and 57.7 of 2 θ value, which was correlated with the β-Bi_2O_3 [Greenwood et al., 1984]. β-Bi_2O_3 is known as an intermediate transition state of α-Bi_2O_3. The result suggests that BiO rather than α-Bi_2O_3 and β-Bi_2O_3 is more preferable to the activity.

5. The Other Instrumental Measurement

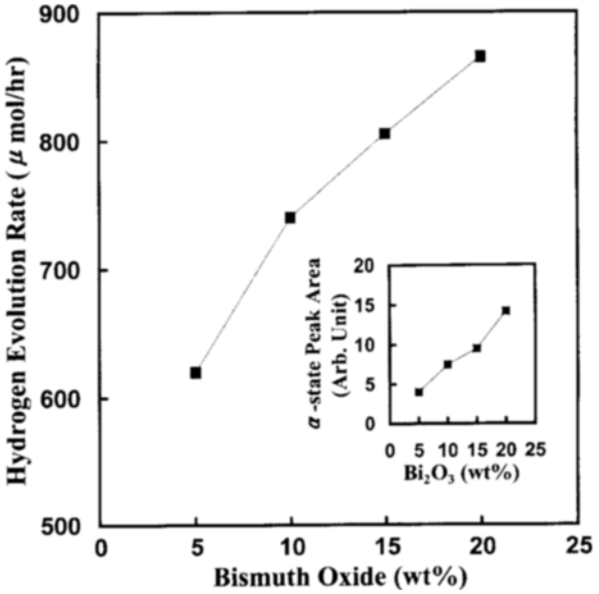

Fig. 6. Rate of hydrogen evolution on xB-R400 catalysts as a function of loading of Bi_2O_3 on TiO_2, xB. The inset shows the relationship between the α-state peak area and the loading of Bi_2O_3 on TiO_2.

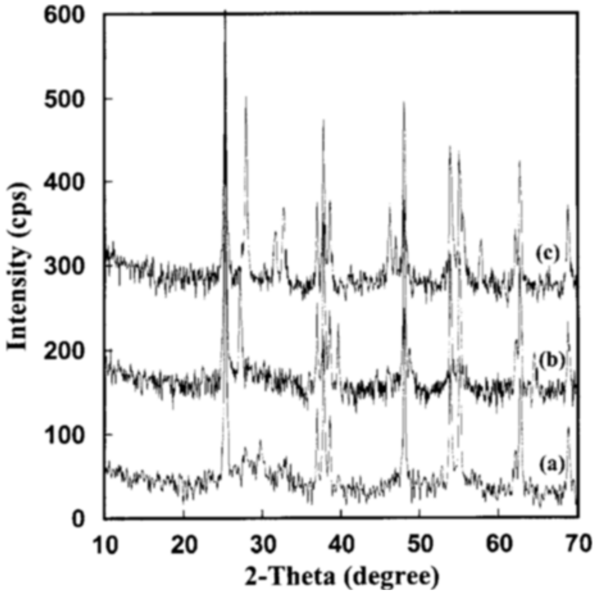

Fig. 7. XRD patterns of various 10 wt% Bi_2O_3/TiO_2 catalysts with different treatments, (a) O500, (b) R400, and (c) R5O4.

From the XPS experiment of 5B-O500, 5B-R400, and 5B-R5O4 catalysts, the binding energy of $Bi(4f_{1/2})$ in O500 catalyst was lower by 0.3 eV compared to the value reported in the handbook (165.3 eV), which was reasonable considering that Bi_2O_3 has well-developed oxygen vacancies. In R 400 catalyst, a more lowered peak of Bi was observed, which indicated that Bi_2O_3 was partially reduced to the state of BiO. Whereas, in R5O4 catalyst, in spite of reoxidation at 400 °C, a lower peak of Bi was still observed even though of lower intensity. It was reported that the composition of Bi/O in oxidation of bismuth film at 175-250 °C under 30 torr oxygen atmosphere was 0.72 resulting at most in the increase of 2 eV of binding energy of Bi [Kofstad, 1972]. This result was qualitatively in good agreement with our XPS data.

To study the shape and the composition of the catalysts, SEM-EDX analysis was performed. Any different characteristic result was not observed among O500, R400, and R5O4 catalysts in SEM photographs. Especially in R400 catalyst, a greater change in the exposed fraction of bismuth on the surface, i.e., to 2.5 mole % for O500 catalyst and to 3.5 mole % for R400 catalyst, was detected from the EDX data. This exposed fraction of bismuth on the surface was thought to be favorable to accept the sulfur-containing molecules as a reactant.

6. The Study of the Adsorptions of Sulfur and Hydroxyl Ion

To determine the main cause of high photocatalytic activity over bismuth oxide on titania in the presence of polysulfide, the adsorption properties of sulfur and hydroxyl ion in solution were studied. The adsorption of sulfur as a reactant is important in the reaction of adsorbed sulfur with a photogenerated hole, i.e., in the oxidation of sulfur resulting in the acceleration of removal of hole. In addition, the adsorption of hydroxyl ion is also important because the surface hydroxyls can play a role in trapping holes.

Fig. 8 shows the amount of sulfur adsorbed on xB-O500 catalyst as a function of loading of bismuth oxide on titania. The amount of sulfur adsorbed increased linearly with the increase of loading of bismuth oxide. Considering only the amount of sulfur adsorbed, the amount of sulfur adsorbed was not correlated with the activity of bismuth oxide as shown in Fig. 3. In this case, the surface coverage of sulfur on the catalyst was calculated from the result of 10 wt% Bi_2O_3/TiO_2. The 10 wt% Bi_2O_3 catalyst has 191 μmol of sulfur and 429 μmol of bismuth per g-catalyst. Therefore, if one bismuth molecule reacts with one polysulfide, at most, 44.5 % of bismuth will be covered with sulfur regardless of the loading of bismuth oxide.

The other factor for controlling the activity was thought to be the amount of hydroxyl ion adsorbed on the catalyst. Fig. 9 shows the amount of surface hydroxyl ion adsorbed on xB-O500 catalyst as a function of loading of bismuth oxide. The amount of surface hydroxyl ion adsorbed decreased with the increase of loading of bismuth oxide. Bismuth oxide on titania was considered to cover the titania surface. In the case of undoped catalyst, the amount of hydroxyl ion on the surface was 96 μmol per g-catalyst. This value was in good agreement with the result reported previously [Anderson, 1975]. From this value the coverage of hydroxyl ion at 10 wt% Bi_2O_3/TiO_2 could be calculated, and the calculated value was 66.7 %. As the loading of bismuth oxide on titania increased, the amount of hydroxyl ion adsorbed on the catalyst decreased resulting in a decrease of the activity. Therefore, considering both the amount of sulfur adsorbed and the amount of hydroxyl ion adsorbed, an optimum loading of bismuth oxide is compromised by the above two opposite factors giving an optimum value of about 5 wt%, as shown in Fig. 3.

Although there were many other factors that could affect the activity, the amount of sulfur adsorbed was most responsible for the activity. Typically, the R400 catalyst showed a relatively high activity and also a large amount of sulfur adsorbed due to the large fraction of bismuth exposed on the catalyst. In the case of R5O4 catalyst, a low activity and a small amount of sulfur adsorbed were observed. It was reported that β-Bi_2O_3 could be formed by oxidation at 220-430 °C under atmospheric pressure of oxygen. It has been known that β-Bi_2O_3 has filled fully with oxygen in the oxygen vacant sites, and from this it has been considered to be a lower fraction of bismuth on the catalyst surface reducing the amount of sulfur adsorbed.

If the main factor for controlling the reaction rate is the amount of sulfur adsorbed, the rate of hydrogen evolution

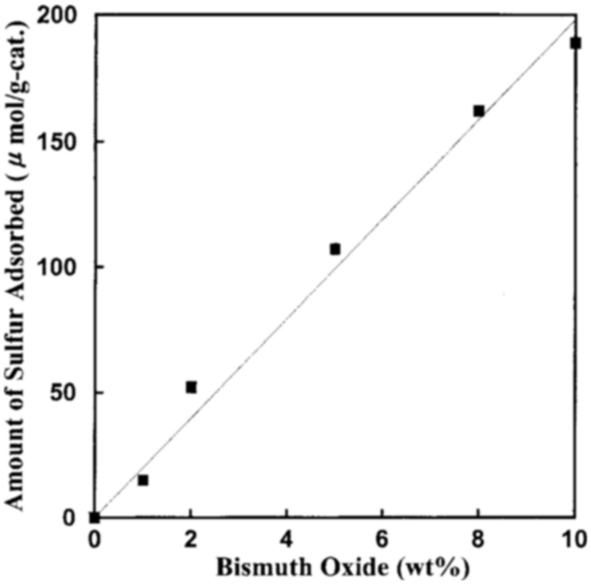

Fig. 8. Amount of sulfur adsorbed on xB-O500 catalyst as a function of loading of Bi_2O_3 on TiO_2, xB.

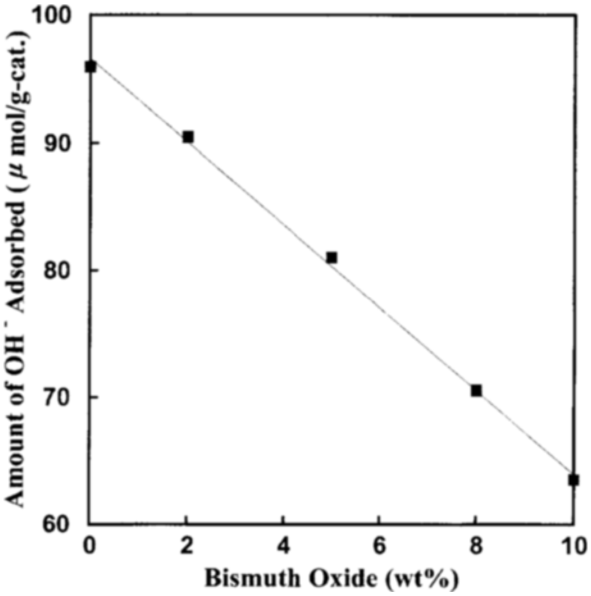

Fig. 9. Amount of hydroxyl ion adsorbed on xB-O500 catalyst as a function of loading of Bi_2O_3 on TiO_2, xB.

should be improved by the increase of catalyst weight because the more exposed the catalyst surface, the more amount of sulfur adsorbed resulting in an increase of the reaction rate. Therefore, we tested the rate of hydrogen evolution as a function of catalyst weight. As a result, the rate of hydrogen evolution rate increased with the amount of catalyst weight proportionally.

CONCLUSIONS

Bismuth oxide on titania as a new sulfur-sensitive photocatalyst was prepared and characterized. The rate of hydrogen evolution was controlled both by the amounts of sulfur adsorbed and of hydroxyl ion adsorbed. The activity was enhanced with increases of the two amounts mentioned above. The amount of sulfur adsorbed increased and that of hydroxyl ion adsorbed decreased with the increase of loading of bismuth oxide on the surface of titania compromising the optimum loading of bismuth oxide. There were two kinds of bismuth oxide--Bi_2O_3 and BiO, and the latter was much more responsible for the activity giving more exposure of bismuth oxide on the surface.

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