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Photocatalytic Reaction of Ethanol over Titanium Diselenide

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A suspension of $TiSe_2$ in ethanol was illuminated with ultraviolet light in an atmosphere of Ar, air, or O_2 at 298 K. The main products were acetaldehyde, acetaldehyde diethyl acetal (acetal), acetic acid, water, hydrogen, ethylene, methane, and carbon dioxide. Each yield of the products under air or O_2 was higher than under Ar, except for that of hydrogen and ethylene. Platinum under an O_2 atmosphere exerted its effect for producing CH_3COOH, acetal, CO_2, CH_3CHO, CH_4, and H_2O, while under Ar it contributed to generating CO_2, CH_4, and H_2. No effect of Pt was observed for generating C_2H_4 under either an atmosphere of Ar or O_2.

Titanium dioxide is well known to act as a photocatalyst for the evolution of H_2 from ethanol in the presence of Pt.[1—6] The author demonstrated that the photocatalytic activity of TiO_2 could be attributed to the active oxygen liberated from the catalyst, and that the reduction of the catalyst due to light illumination caused a lowering of the activity of TiO_2 in the absence of Pt under an atmosphere of Ar.[7]

On the other hand, since $TiSe_2$ has no oxygen in its molecule, it is possible to imagine that the catalyst is free from any drop in its photocatalytic activity due to the liberation of active oxygen. Even though $TiSe_2$ has a semi-metallic character,[8] we have mentioned that the catalyst acts as a photocatalyst.[9] However, no instance has been completely elucidated concerning the photocatalytic formation of all the products from ethanol and its mechanism by using $TiSe_2$, except for the formation of H_2 and CH_3CHO by the authors.[9]

Platinum on a catalyst promotes a charge separation of the electrons and holes formed on the catalyst by light illumination because of the electron-withdrawing ability with Pt.[10,11] Such a charge separation favors the release of hydrogen from ethanol over Pt/TiO_2.[1—6] However, no instance of $TiSe_2$ has yet been reported concerning any effect due to the addition of platinum.

Oxygen is well-known as an electron-capture material.[12—14] A photocatalytic reaction is initiated with the electron and hole formed on a catalyst by light illumination. It is therefore presumed that oxygen has an effect on the photocatalytic reaction. However, no report has demonstrated such an effect with oxygen on all products from ethanol with $TiSe_2$, except that regarding the formation of CH_3CHO and H_2 by the authors.[9]

This study was aimed at examining the catalytic activity of $TiSe_2$, itself, the effect due to the addition of Pt, and the influence of the atmosphere. We were also interested in the detailed mechanism concerning all of the products formed from ethanol upon light illumination.

Experimental

The experimental conditions were the same as those published previously.[9)]

Photocatalyst. The $TiSe_2$ used was 30 mg, 99.8%, 300 mesh, Furuuchi Chemical Co., Ltd. The effect of the Pt was examined by adding 1.5 mg (5 wt% of the $TiSe_2$ used) of Pt powder (99.99%, 350 mesh, Mitsuwa Chemical Co., Ltd.) to the $TiSe_2$ powder.

Ethanol. Commercial C_2H_5OH (2.0 ml, 99.5%, special grade, Katayama Chemical Co., Ltd.) was used which had been purified by distillation after drying over CaO.

Reaction Procedure. The catalyst and a stirring bar were placed in a Pyrex glass tube (13 mmϕ×100 mm); the tube was then sealed with a small-bored screw cap with a silicone liner coated with Teflon after removing the air by blowing Ar or O_2 into the tube for 20 min. Such a removal of air was omitted in the case of an atmosphere of air. After the tube was turned upside down, ethanol was injected into it through the silicone liner with a microliter syringe.

Illumination for each suspension of 30 mg of $TiSe_2$ in 2.0 ml of C_2H_5OH with a 400 W high-pressure mercury lamp (UVL-400 HB, Riko-Kagaku Sangyo Co., Ltd.) was performed with stirring magnetically at a distance of 7.5 cm from the center of the lamp in a water tank (a Riko RH400-10 W photochemical reactor) maintained at 298 K, by circulation of cold distilled water. After illumination, the reaction tube was immediately transferred to a beaker containing ice-water and was kept for about 15 min in a refrigerator. This was because the produced CH_3CHO should be kept in the liquid-phase as much as possible and also be kept in the dark.

Analysis. A Shimadzu GC-8A gas chromatograph (activated charcoal, 60—80 mesh, 3 mmϕ×3 m stainless-steel column, 393 K, N_2 carrier, TCD) was used to analyze the gaseous products. Acetaldehyde, acetal, and water were analyzed using a Shimadzu GC-4B gas chromatograph (PEG-6000 10%, Flusin P, 30—60 mesh, 3 mmϕ×3 m stainless-steel column, 333 K, He carrier, TCD). Formaldehyde was analyzed by a Shimadzu GC-4B gas chromatograph (APS-201 20%, Flusin T, 60—80 mesh, 3 mmϕ×2.5 m stainless-steel column, 363 K, He carrier, TCD). Subsequently, acetic acid was analyzed by a Perkin–Elmer 900 gas chromatograph (PEG-6000 10%, Flusin P, 30—60 mesh, 2 mmϕ×1.8 m glass column, 413 K, N_2 carrier, FID).

Results and Discussion

Figure 1 shows the formation of acetaldehyde from a suspension of $TiSe_2$ or $Pt/TiSe_2$ in ethanol under an Ar or O_2 atmosphere. The yield of CH_3CHO with $Pt/TiSe_2$ under Ar was higher than that[9] without Pt.

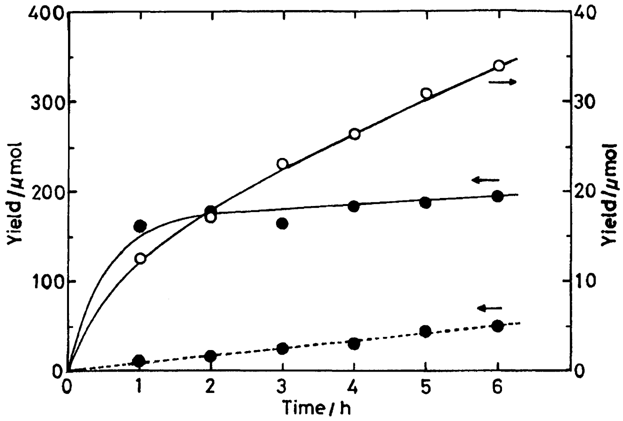

Fig. 1. Formation of acetaldehyde vs. the illumination time for a suspension of 30 mg of $TiSe_2$ or Pt (1.5 mg)/$TiSe_2$ in 2.0 ml of C_2H_5OH under an Ar (○) or O_2 (●) atmosphere. ---: $TiSe_2$, —: Pt/$TiSe_2$.

The reason for this observation may be explained by an electron transfer to Pt.[10,11] First, e^- and h^+ are formed by illuminating a catalyst,[14]

$$TiSe_2 \rightarrow e^- + h^+. \tag{1}$$

The h^+ formed gives CH_3CHO and H^+ from C_2H_5OH,

$$C_2H_5OH + 2h^+ \rightarrow CH_3CHO + 2H^+. \tag{2}$$

The H^+ formed is utilized for the evolution of H_2, as described later. The reaction of Eq. 2 proceeds very smoothly under Ar, since the e^- formed on $TiSe_2$ (Eq. 1) is drawn toward the Pt; this drawing of the e^- prevents any recombination reaction of e^- and h^+.

The yield of CH_3CHO with $TiSe_2$ under O_2 was higher than that[9] under Ar. The yield of CH_3CHO with Pt/$TiSe_2$ under O_2 was also higher than that under Ar. These results may be explained by capturing electrons with oxygen, since oxygen is known to capture electrons.[12—14] The e^- formed in Eq. 1 is captured by an oxygen molecule,

$$O_2 + e^- \rightarrow O_2{}^-. \tag{3}$$

Acetaldehyde is formed in the same manner as in the mechanism for the photoxidation of 2-propanol over TiO_2 reported by Bickley et al.,[12] e.g., in the transfer of a proton from ethanol to the O_2^- formed in Eq. 3, as follows:

$$C_2H_5OH + O_2{}^- \rightarrow C_2H_5O^- + HO_2{}^{\bullet}, \tag{4}$$

$$C_2H_5OH + HO_2{}^{\bullet} \rightarrow C_2H_5O^{\bullet} + H_2O_2, \tag{5}$$

$$C_2H_5O^- + H_2O_2 \rightarrow CH_3CHO + H_2O + OH^{\bullet} + e^-, \tag{6}$$

and

$$C_2H_5O^{\bullet} + OH^{\bullet} \rightarrow CH_3CHO + H_2O. \tag{7}$$

These reactions expressed by Eqs. 3, 4, 5, 6, and 7 can be summarized as follows:

$$2C_2H_5OH + O_2 \rightarrow 2CH_3CHO + 2H_2O. \tag{8}$$

Water was, in fact, produced in greater quantity under air than under Ar. In an H-atom transfer from ethanol to O_2^- (form $C_2H_5O^{\bullet}$ and HO_2^-), the overall reaction is the same as expressed by Eq. 8. That is to say, CH_3CHO is produced via a $C_2H_5O^{\bullet}$ radical or a $C_2H_5O^-$ anion. In brief, CH_3CHO is formed only according to Eq. 2 under Ar, while it is produced according to either Eq. 2 or Eq. 8 under an O_2 atmosphere.

To make sure of such a mechanism, the remaining O_2 in the reaction tube was examined during a photocatalytic reaction of the suspension under an O_2 atmosphere (Fig. 2). A linear decreasing curve for the content of O_2 when $TiSe_2$ was used, in fact, agreed with the linear increasing curve for the yield of CH_3CHO with $TiSe_2$ under O_2. When using Pt/$TiSe_2$ under O_2, the curve expressing the content of O_2 undergoes a considerable decrease during the initial illumination; the fact that there was no large decrease after the illumination is also consistent with the curve for the yield of CH_3CHO accompanying a significant increase up to the initial illumination and the gradual increase after illumination. That is to say, each yield of CH_3CHO under O_2 with either $TiSe_2$ or Pt/$TiSe_2$ can be accounted for by such a decrease in the O_2 content.

Figure 3 shows the evolution of H_2 from a suspension of $TiSe_2$ or Pt/$TiSe_2$ in ethanol under an Ar or O_2 atmosphere. In the absence of Pt, the yield of H_2 under O_2 was much lower than that[9] under Ar, and was the same as that[9] under air. In the presence of Pt under Ar, the evolution of H_2 was about twice that[9] without Pt, as mentioned in the previous paper. This may be explained by the fact that Pt draws the e^- formed by illumination with light, as shown in Eq. 1. Such an action of Pt prevents any recombination of the e^- and h^+ expressed in Eq. 1.[10,11] Therefore, under an Ar at-

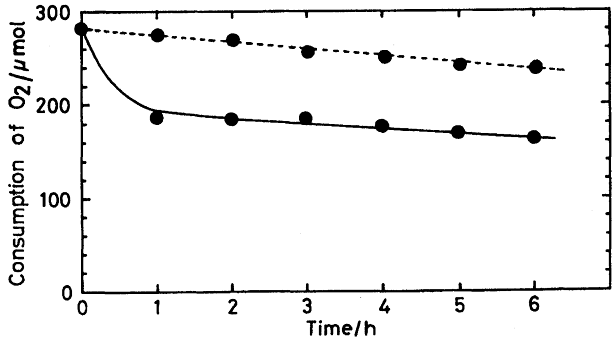

Fig. 2. Remaining amount of O_2 in the reaction tube vs. the illumination time for a suspension of 30 mg of $TiSe_2$ or Pt (1.5 mg)/$TiSe_2$ (30 mg) in 2.0 ml of C_2H_5OH under O_2 atmosphere. ---: $TiSe_2$, —: Pt/$TiSe_2$.

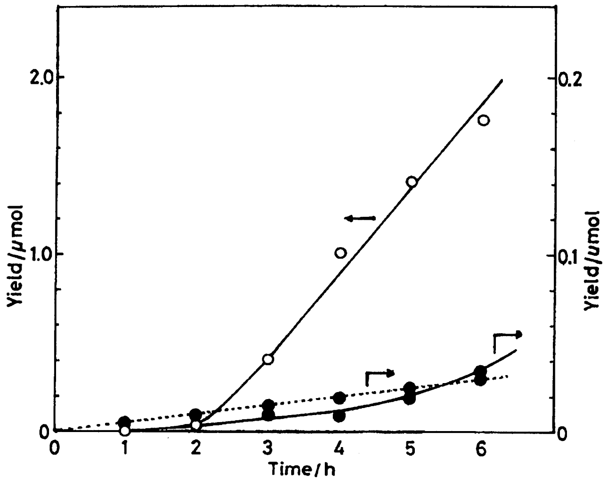

Fig. 3. Evolution of H_2 vs. the illumination time for a suspension of 30 mg of $TiSe_2$ or Pt (1.5 mg)/$TiSe_2$ in 2.0 ml of C_2H_5OH under an Ar (○) or O_2 (●) atmosphere. ---: $TiSe_2$, —: Pt/$TiSe_2$.

mosphere, Pt favors the evolution of H_2 from the e^- as expressed in Eq. 1 and H^+ in Eq. 2,

$$2H^+ + 2e^- \rightarrow H_2. \qquad (9)$$

On the other hand, under an atmosphere of O_2, no Pt effect was observed during 5 h of illumination. Electron capture due to $O_2^{12-14)}$ may be offered to explain the absence of a Pt effect under O_2. The e^--deficient conditions due to this electron capture inhibit the evolution of H_2 expressed in Eq. 9. In fact, as can be seen from Figs. 2 and 3, the effect due to the addition of Pt was gradually developed when the O_2 content in the reaction tube approached a minimum at 6 h of illumination.

It should also be noted hydrogen is evolved from the e^- and H^+ formed at Eqs. 1 and 2, respectively, as shown in Eq. 9. After all, H_2 and CH_3CHO are produced by the following reaction reported by Sakata and Kawai:1)

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \qquad \Delta G^\circ = 41.0 \text{ kJ mol}^{-1} \qquad (10)$$

Hydrogen in amounts equimolar with CH_3CHO should therefore be evolved. However, the molar quantity of the H_2 evolved, under each atmosphere of Ar or O_2, was much lower than that of the CH_3CHO formed, as can be seen from Figs. 1 and 3. In an O_2 atmosphere, CH_3CHO may be formed by the oxidation of C_2H_5OH with oxygen, as shown in Eq. 8, while it is not produced by oxidation under an atmosphere of Ar. Therefore, a possible cause for such a lower molar ratio of H_2/CH_3CHO under Ar is the formation of CH_3CHO by the oxidation of C_2H_5OH with $TiSe_2$, in the same mechanism as was previously demonstrated concerning the oxidation of C_2H_5OH with TiO_2,7) as follows:

$$C_2H_5OH + 2TiSe_2 \rightarrow CH_3CHO + Ti_2Se_3 + H_2Se \qquad (11)$$

and

$$C_2H_5OH + TiSe_2 \rightarrow CH_3CHO + TiSe + H_2Se. \qquad (12)$$

The CH_3CHO formed according to Eqs. 11 and 12 contributes to a lowering of the H_2/CH_3CHO ratio. A bad smell resembling that of H_2Se was actually perceived when the screw cap was opened.

Figure 4 shows the formation of acetal from a suspension of $TiSe_2$ or Pt/$TiSe_2$ in ethanol under an O_2 atmosphere. Although there was no large difference between the yield of CH_3CHO under O_2 and that9) under air, acetal was formed only under O_2 atmosphere. Acetal with either Pt/$TiSe_2$ or $TiSe_2$ was formed about 0.1 times that of CH_3CHO, as can be seen Figs. 1 and 4. Although the yield of CH_3CHO with Pt/$TiSe_2$ or $TiSe_2$9) under Ar was lower than that under O_2, it suffices for the formation of acetal because of the acetal/CH_3CHO ratio mentioned above. However, under Ar, acetal was not formed when using either $TiSe_2$ or Pt/$TiSe_2$. Acetal was also not formed under air with $TiSe_2$. It is therefore evident that much O_2 is required for the formation of acetal.

Accordingly, acetal is probably formed by the following abbreviated equation through a proton transfer from C_2H_5OH to the O_2^-, as expressed in Eq. 3:

$$CH_3CHO + 2C_2H_5OH \rightarrow CH_3CH(OC_2H_5)_2 + H_2O. \qquad (13)$$

Under O_2, Pt contributed highly to producing acetal. The higher yield of CH_3CHO with Pt/$TiSe_2$ than that with $TiSe_2$ seems to be the reason for this result.

Figure 5 shows the formation of acetic acid from a suspension of $TiSe_2$ or Pt/$TiSe_2$ in ethanol under an air or O_2 atmosphere. The identification of CH_3COOH must be carried out cautiously, since a slight amount of CH_3COOH is almost adsorbed on the surface of the analysis path of the gas chromatograph because of the high adsorptive property of the acid, and it is no detectable. The lower limit of detection was about 0.6 μmol in the present experiment. The use of Pt/$TiSe_2$ gave trace amounts of CH_3COOH under Ar. On the contrary, CH_3COOH was not detected in the absence of Pt under Ar; however, it seems reasonable to assume

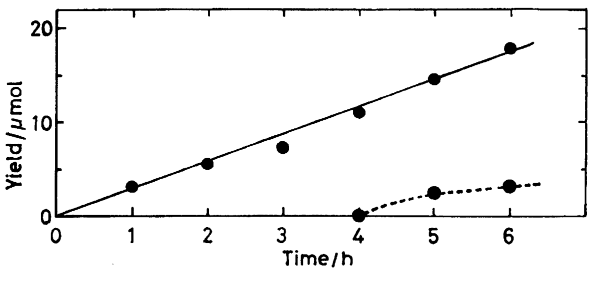

Fig. 4. Formation of acetal vs. the illumination time for a suspension of 30 mg of $TiSe_2$ or Pt (1.5 mg)/$TiSe_2$ in 2.0 ml of C_2H_5OH under an O_2 (●) atmosphere. ---: $TiSe_2$, —: Pt/$TiSe_2$.

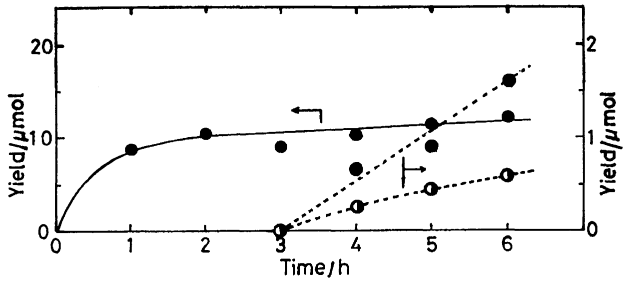

Fig. 5. Formation of acetic acid vs. the illumination time for a suspension of 30 mg of $TiSe_2$ or Pt (1.5 mg)/$TiSe_2$ in 2.0 ml of C_2H_5OH under an air (◑) or O_2 (●) atmosphere. ---: $TiSe_2$, —: Pt/$TiSe_2$.

that a slight amount of CH_3COOH was produced in practice, since if a slight amount of the acid exists in the reaction solution after decomposition to CH_4 and CO_2, its detection is difficult because of the detection limit shown above. This is also supported by the evolution of CH_4 and CO_2 described later.

Judging from the much higher yield of CH_3COOH under air or O_2 than Ar, CH_3COOH is probably produced by the following two routes. Under an air or O_2 atmosphere, CH_3COOH predominantly produces via further oxidation of CH_3CHO by the O_2^- formed in Eq. 3 as follows:

$$CH_3CHO + O_2{}^- \rightarrow CH_3CO^- + HO_2{}^\bullet, \qquad (14)$$

$$CH_3CHO + HO_2{}^\bullet \rightarrow CH_3CO^\bullet + H_2O_2, \qquad (15)$$

$$CH_3CO^- + H_2O_2 \rightarrow CH_3COOH + OH^\bullet + e^-, \qquad (16)$$

and

$$CH_3CO^\bullet + OH^\bullet \rightarrow CH_3COOH. \qquad (17)$$

The following equation is therefore obtained from Eqs. 3, 14, 15, 16, and 17:

$$2CH_3CHO + O_2 \rightarrow 2CH_3COOH. \qquad (18)$$

Under Ar, CH_3COOH is formed from CH_3CHO and H_2O according to the mechanism proposed by Sakata and Kawai concerning the use of TiO_2,[1)]

$$CH_3CHO + H_2O \rightarrow CH_3COOH + H_2 \qquad \Delta G^\circ = -18.9 \text{ kJ mol}^{-1}, \qquad (19)$$

where H_2O is contained as a small amount of impurity in ethanol. It is provided according to Eqs. 8 and 13.

Figure 6 shows the evolution of CH_4 from a suspension of $TiSe_2$ or Pt/$TiSe_2$ in ethanol under an Ar, air, or O_2 atmosphere. A small amount of CH_4 was evolved under each atmosphere of Ar, air, or O_2. Two paths are possible for the evolution of CH_4. First, CH_4 is directly evolved from C_2H_5OH,

$$C_2H_5OH \rightarrow CH_4 + HCHO. \qquad (20)$$

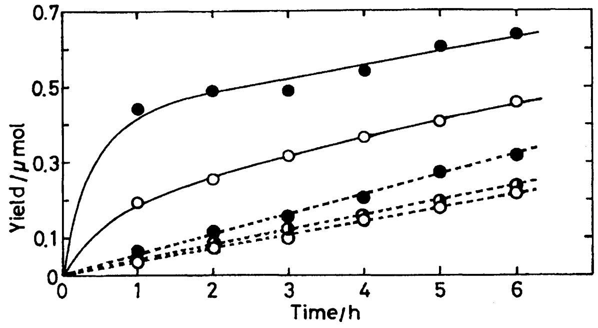

Fig. 6. Evolution of CH_4 vs. the illumination time for a suspension of 30 mg of $TiSe_2$ or Pt (1.5 mg)/$TiSe_2$ in 2.0 ml of C_2H_5OH under an Ar (○), air (◑), or O_2 (●) atmosphere. ---: $TiSe_2$, —: Pt/$TiSe_2$.

To make sure of this reaction, although the formation of HCHO was analyzed by gas chromatography, no HCHO (under Ar) was detected in the use of either $TiSe_2$ or Pt/$TiSe_2$. A second and, perhaps, more likely route would be the evolution of CH_4 from CH_3COOH by the photo-Kolbe-type reaction proposed by Kraeutler and Bard,[15)]

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad \Delta G^\circ = -55.8 \text{ kJ mol}^{-1}. \qquad (21)$$

The molar ratio of CH_4/CO_2 should be 1, as can be seen in Eq. 21. The evolution of CO_2 is shown in Fig. 7 in order to comfirm this ratio. As can be seen Figs. 6 and 7, Pt/$TiSe_2$ under Ar obtained $CH_4/CO_2=1$. The lower molar ratio of CH_4/CO_2 than 1 was obtained when using Pt/$TiSe_2$ under O_2, and $TiSe_2$ under an O_2 or air atmosphere. This observation is consistent with the fact

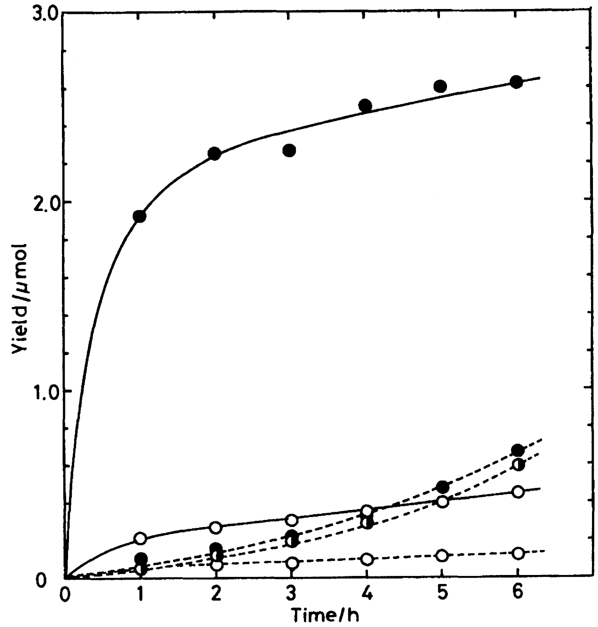

Fig. 7. Evolution of CO_2 vs. the illumination time for a suspension of 30 mg of $TiSe_2$ or Pt (1.5 mg)/$TiSe_2$ in 2.0 ml of C_2H_5OH under an Ar (○), air (◑), or O_2 (●) atmosphere. ---: $TiSe_2$, —: Pt/$TiSe_2$.

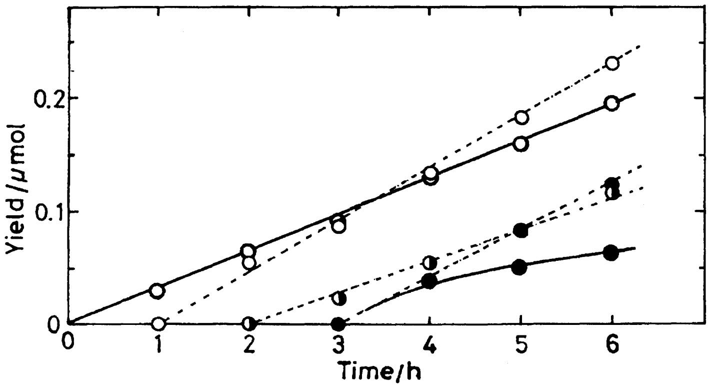

Fig. 8. Evolution of C_2H_4 vs. the illumination time for a suspension of 30 mg of $TiSe_2$ or Pt (1.5 mg)/$TiSe_2$ in 2.0 ml of C_2H_5OH under an Ar (○), air (◑), or O_2 (●) atmosphere. ---: $TiSe_2$, —: Pt/$TiSe_2$.

that CO_2 is the final oxidation product of C_2H_5OH. The use of $TiSe_2$ under Ar gave a higher molar ratio of CH_4/CO_2 than 1. This is in conflict with the evolution of CH_4 by the photo-Kolbe reaction. It is unknown why such a higher molar ratio was obtained, and further experimentation is thus necessary to explain this result.

Under O_2, since trace amounts of HCHO were detected in the use of $TiSe_2$ or Pt/$TiSe_2$, it appears to be formed according to Eq. 20. However, since this direct evolution of CH_4 is negligibly small because of trace amounts of the CH_4 evolution, CH_4 is predominantly evolved from CH_3COOH by the photo-Kolbe reaction expressed by Eq. 21.

Figure 8 shows the evolution of C_2H_4 from a suspension of $TiSe_2$ or Pt/$TiSe_2$ in ethanol under an Ar, air, or O_2 atmosphere. Ethylene (as well as H_2) was a product with the higher yield under Ar than that under an air of O_2 atmosphere. Two explanations may be offered for this observation. First, C_2H_4 is given from the CH_3CHO formed in Eq. 2 and the e^- formed in Eq. 1:

$$CH_3CHO + 2e^- \rightarrow C_2H_4 + O^{2-}. \tag{22}$$

This O^{2-} and the H^+ formed in Eq. 2 give water, as follows:

$$2H^+ + O^{2-} \rightarrow H_2O. \tag{23}$$

The following abbreviated equation is formulated using Eqs. 2, 22, and 23,

$$C_2H_5OH + 2h^+ + 2e^- \rightarrow C_2H_4 + H_2O. \tag{24}$$

Under an O_2 or air atmosphere, Eq. 22 becomes difficult due to the capture of electrons with O_2;[12—14] the evolution of C_2H_4 under O_2 or air was therefore lower than that under Ar. A second explanation is the oxidation of C_2H_4 with O_2, judging from the higher formation of CO_2 and H_2O corresponding to the final oxidation product of C_2H_4 under O_2 or air than that under Ar. However, this presumption should be made while considering the formation of H_2O and CO_2 according to Eqs. 8, 13, and 21.

Although Pt is a material which is used to aid in the charge separation of the e^- and h^+ formed according to Eq. 1,[10,11] the addition of Pt under Ar gave no increase in the yield of C_2H_4, in contrast to some increase in those of CH_3CHO and H_2. That such an effect of charge separation is used to form CH_3CHO (Eq. 2) and H_2 (Eq. 9) seems to be the reason for this observation.

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