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Relationship between the Yields of Products from Ethanol over Titanium Dioxide and the Quantity of Light

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Acetaldehyde, acetaldehyde diethyl acetal (acetal), ethylene, hydrogen, methane, and carbon dioxide were produced from neat ethanol over TiO_2 powder without metal in an Ar atmosphere under light irradiation. The yields of these products decreased in the above order. The following observation was obtained by using a filter which cut light at wavelengths below 390 nm. The yield of carbon dioxide was slightly decreased. The yield of acetaldehyde was greatly decreased at the initial irradiation, while it was slightly decreased with continuing of irradiation. The yield of acetal somewhat decreased, and that of ethylene, methane, and hydrogen roughly decreased to 1/2, 1/5, and 1/10, respectively.

A photocatalytic reaction with a semiconductor has been studied for the photochemical conversion of solar energy. For this purpose, under an oxygen-free atmosphere, many authors have reported on the photocatalytic evolution of H_2 from a mixture of aliphatic alcohols and water[1—6] or neat aliphatic alcohols[2—5,7] over platinized titanium dioxide powder (Pt/TiO_2). There have been a few reports on the photocatalytic H_2 evolution from C_2H_5OH in aqueous[1] or from neat C_2H_5OH[8] over TiO_2 alone without loading metal under an oxygen-free atmosphere.

Under an oxygen-free atmosphere, a mixture of C_2H_5OH and H_2O over Pt/TiO_2 produces CH_3CHO,[1,3,4] CH_3COOH,[1] CH_4,[1] and CO_2.[1] Neat C_2H_5OH over Pt/TiO_2 powder produced CH_3CHO,[5,7] acetaldehyde diethyl acetal (acetal),[5,7] and CO_2.[5] Ethanol over TiO_2 powder in an aqueous solution of silver salts produced CH_3CHO.[9] One of the authors noticed the evolution of C_2H_4 from neat C_2H_5OH over TiO_2 alone without loading metal.[8] These studies show that C_2H_5OH under an oxygen-free atmosphere produces H_2, CH_3CHO, acetal, CH_3COOH, CH_4, CO_2, and C_2H_4. All of the above reports have been rarely discussed concerning a quantitative description of all of the products from C_2H_5OH.

It is presumed that photocatalytic reactions depend on the quantity of light. However, no instance has yet been reported concerning the relationship between the yields of all products from C_2H_5OH and the quantity of light. Titanium dioxide is reduced by such reductants as alcohols in an O_2-free atmosphere.[6,10] If Pt is deposited on TiO_2, to determine the catalytic activity of the oxide becomes difficult, since the reduction of TiO_2 is depressed by Pt.[6] Therefore, we examined the above relationship with TiO_2 alone without loading Pt.

Experimental

Photocatalyst. The TiO_2 photocatalyst (99.9%, 300 mesh, 1.9 $m^2 g^{-1}$, Furuuchi Chemical Co., Ltd.) was used without any treatment, such as reduction or evacuation. The TiO_2 was a mixture of rutile and about 15% anatase. The specific surface of TiO_2 area was measured by the BET method using a Shimadzu physical adsorption analyzer (AccuSorb 2100-01). The crystal form of TiO_2 was identified by an X-ray diffraction analysis using a Rigaku Denki X-ray diffractometer (RAD-1VC).

Ethanol. The commercial C_2H_5OH (99.5%, special grade, Katayama Chemical Co., Ltd.) used was purified by distillation after drying over CaO.

Reaction Procedure. A weighed quantity of the TiO_2 (30 mg) was placed directly in a Pyrex glass (passes light of wavelengths longer than 230 nm) tube (13 mm$\phi \times$100 mm) in which a stirring bar was placed, without any treatment, such as mixing by an agate mortar; the tube was then sealed with a small-bored screw cap with a silicone liner coated with Teflon after removing air by blowing Ar into the tube for 20 min. After the tube had been turned upside down, ethanol (2.0 ml) was injected into it through a silicone liner with a microliter syringe.

Each suspension consisting of TiO_2 (30 mg) and C_2H_5OH (2.0 ml) was irradiated with light of full wavelengths by using a 500-W xenon lamp (UXL-500D, Ushio Inc.) with stirring magnetically. The distance between the reaction tube and the lamp was 10 cm. The light intensity at the reaction tube was 10.5 mW cm^{-2} (without a filter) or 3.2 mW cm^{-2} (with the filter shown below), and was measured by an Ushio actinometer (UIT-101, UVD-405PD). Light was filtered by a colored glass filter (L-42, Toshiba Corp.) which cut light with wavelengths shorter than 390 nm. The transmittance of light with this filter was 5% at near 400 nm, 20% at 410 nm, and 50% at 420 nm. No product from C_2H_5OH was observed in the absence of light or a catalyst.

Analysis of Products. All of the products were analyzed by gas chromatography after a reaction tube irradiated was immediately transferred to a beaker containing ice-water and was kept for about 15 min in a refrigerator. This was because the CH_3CHO produced should be kept in the liquid-phase as much as possible. A Shimadzu GC-8A gas chromatograph (activated charcoal, 60—80 mesh, 3 mm$\phi \times$3 m stainless-steel column, 393 K, N_2 carrier, TCD) was used for analyzing the gaseous products. After an analysis of the gaseous products, the tube was turned upside down; the suspension separated into a TiO_2-and-ethanol solution by centrifugation for an analysis of the liquid products. The liquid products, except CH_3COOH and HCHO, were analyzed by using a Shimadzu GC-4B gas chromatograph (PEG-6000 10%, Flusin P, 30—60 mesh, 3 mm$\phi \times 3$ m stainless-steel column, 333 K, He carrier, TCD). Acetic acid was analyzed by a Perkin–Elmer 900 gas chromatograph (PEG-6000 10%, Flusin P, 30—60 mesh, 2 mm$\phi \times 1.8$ m glass column, 413 K, N_2 carrier, FID). Subsequently, HCHO was analyzed by a Shimadzu GC-8A gas chromatograph (APS-201 20%, Flusin T, 60—80 mesh, 3 mm$\phi \times 2.5$ m stainless-steel column, 363 K, He carrier, TCD).

Results and Discussion

Acetaldehyde and Acetal. When TiO_2 is irradiated by light with wavelengths below 410—387 nm corresponding to its band gap energy (BG) of 3.0—3.2 eV,[11—18] e^- and h^+ are formed,[11,16,17,19—22]

$$TiO_2 \rightarrow e^- + h^+. \tag{1}$$

The h^+ and e^- formed produce acetaldehyde and hydrogen,

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

$$2H^+ + 2\ e^- \rightarrow H_2. \tag{3}$$

The following equation is obtained from Eqs. 2 and 3:

$$C_2H_5OH + 2\ h^+ + 2\ e^- \rightarrow CH_3CHO + H_2, \quad \Delta G^\circ = 47.2\ \mathrm{kJ\,mol^{-1}}. \tag{4}$$

All values of ΔG° were calculated from $\Delta_f G^\circ$[23] in a handbook. Although hydrogen is also evolved by the 21 (shown later), its yield is much less than that of CH_3CHO. Such a slight amount of H_2 may be neglected. Therefore, the yield of CH_3CHO should be equal to that of H_2, as can be seen Eq. 4. However, the yield of CH_3CHO shown in Fig. 1 was much higher than that of H_2 shown in Fig. 2. This result agreed with the result[6] in the dehydrogenation of 2-propanol over TiO_2. The reason why the formation of CH_3CHO was much higher than that of H_2 could not be explained without considering that of CH_3CHO by other routes, except for Eq. 4. It is known that when TiO_2 without deposited Pt is used for the photocatalytic reaction of alcohols, the oxide is reduced by the alcohols under an O_2-free atmosphere[6,10] with a blue/gray color change.[5,6,10] Such a color change of irradiated TiO_2 was also observed in the present work. Thus, most of the acetaldehyde is formed by the following equation:

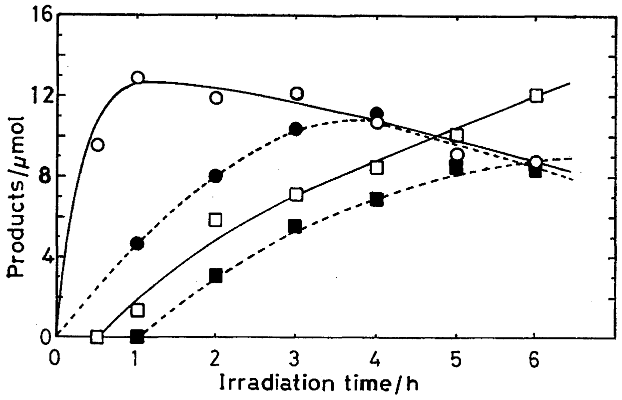

Fig. 1. Formation of acetaldehyde and acetal from a suspension of ethanol (2.0 ml) and TiO_2 (30 mg) under an Ar atmosphere. ○ and ●: acetaldehyde, □ and ■: acetal, —: without a colored glass filter, ····: with a colored glass filter.

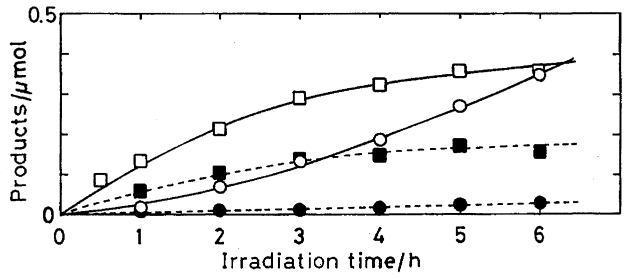

Fig. 2. Formation of H_2 and C_2H_4 from a suspension of ethanol (2.0 ml) and TiO_2 (30 mg) under an Ar atmosphere. ○ and ●: H_2, □ and ■: C_2H_4, —: without a colored glass filter, ····: with a colored glass filter.

$$C_2H_5OH + 2\ TiO_2 \rightarrow CH_3CHO + Ti_2O_3 + H_2O. \tag{5}$$

As Fig. 1 shows, CH_3CHO, which is the most abundant product, yielded with a great increase at the early stages of irradiation; in time its yield gradually decreased with the irradiation time. It seems reasonable to assume that this decrease is caused by a CH_3CHO consumption for the formation of products. Acetal is presumed to be the most possible product, since it is not only the product[5,7] from CH_3CHO (shown in Eq. 10), but the abundant product secondary to the aldehyde. This assumption is supported by the following observation. During the initial irradiation, the yield of acetal is lower than that of CH_3CHO; as the irradiation proceeds it becomes higher than that of the CH_3CHO. Acetal is not formed upon the initial irradiation, because the accumulation of CH_3CHO is essential for the formation of acetal. It is therefore assumed that acetal is formed in the following way:

$$2C_2H_5OH + 2h^+ \rightarrow 2C_2H_5O\cdot\ + 2H^+, \tag{6}$$

$$CH_3CHO + 2e^- \rightarrow CH_3CH\cdot\ + O^{2-}, \tag{7}$$

$$CH_3CH\cdot\ + 2C_2H_5O\cdot \rightarrow CH_3CH(OC_2H_5)_2, \tag{8}$$

$$2H^+ + O^{2-} \rightarrow H_2O. \tag{9}$$

These four equations (from Eq. 6 to Eq. 9) can be summarized as follows:

$$2C_2H_5OH + CH_3CHO + 2h^+ + 2e^- \rightarrow CH_3CH(OC_2H_5)_2 + H_2O. \tag{10}$$

Accordingly, after a certain irradiation time, CH_3CHO was decreased for producing acetal.

When a filter was used, the yield of CH_3CHO was lower than that without the filter, through about 4 h of irradiation. This is because the filtration of light with wavelengths below 390 nm causes a decrease in the formation of h^+ and e^- at Eq. 1 due to decreasing photons, and hinders the reaction of Eq. 4. However, the yield of CH_3CHO was slightly decreased by the use of the filter through irradiation for over 4 h. The most possible cause of this interesting observation can be explained by the utilization of CH_3CHO due to the formation of acetal, since the acetal is the only major product which consumes the CH_3CHO, as mentioned above. Within 4 h of irradiation, the degree of the increase in the yield of acetal with the filter is almost the same as that without it. That is to say, the degree of utilization of CH_3CHO due to the formation of acetal is little altered by the filter within 4 h of irradiation. However, at irradiation for over 4 h, the degree of the increase in the yield of acetal with the filter is lower than that without it. Such a small degree of increase in the formation of acetal causes a slight consumption of CH_3CHO. Therefore, there exists a slight difference between the yield of CH_3CHO without the filter and that with it. This interpretation is supported by that (described later) the sum of the yields of CH_3CHO and acetal agreed with the found decrease for C_2H_5OH.

Hydrogen and Ethylene. The yield of H_2 was not decreased with increasing the irradiation time, in contrast to that of CH_3CHO. This means that H_2 is not consumed for the formation of any products. The evolution of H_2 decreased below about 1/10 at 6 h of irradiation (Fig. 2) by use of a filter. The decreasing photons due to filtration seems to be the reason for this decrease. As can be understood from Eq. 4, decreasing the formation of holes and electrons in Eq. 1 lowers the evolution of H_2.

The following possible route is considered for the evolution of C_2H_4:

$$C_2H_5OH + h^+ \rightarrow C_2H_5O\cdot + H^+, \tag{11}$$

$$C_2H_5O\cdot \rightarrow C_2H_4 + OH\cdot\ , \tag{12}$$

$$H^+ + e^- \rightarrow H\cdot\ , \tag{13}$$

$$OH\cdot + H\cdot \rightarrow H_2O. \tag{14}$$

The following equation is therefore obtained by these four equations from 11 to 14:

$$C_2H_5OH + h^+ + e^- \rightarrow C_2H_4 + H_2O.$$
$$\Delta G^\circ = 6.1\ \text{kJ mol}^{-1}. \tag{15}$$

Figure 2 shows that the evolution of C_2H_4 was reduced to about one-half its initial value by using the filter. This may be explained by decreasing h^+ and e^- due to filtration. When light with wavelengths below 390 nm is filtered, h^+ and e^- at Eq. 1 decrease. This filtration causes a slow reaction of Eq. 15, and the evolution of C_2H_4 decreased.

Methane and Carbon Dioxide. It is reported that CH_4 and CO_2 are evolved from CH_3COOH by "photo-Kolbe reaction",[1,24,25]

$$CH_3COOH \rightarrow CH_4 + CO_2$$
$$\Delta G^\circ = -54.8\ \text{kJ mol}^{-1}. \tag{16}$$

Acetic acid is formed in the following manner, since it is produced from CH_3CHO and H_2O under an O_2-free atmosphere:[1]

$$2H_2O + 2h^+ \rightarrow 2\ \cdot OH + 2H^+,^{26)} \tag{17}$$

in the presence of air, O_2 accepts e^-;[26] however, in the present experiment under an Ar atmosphere, the e^- was not captured by O_2 and evolved H_2 by capturing H^+:

$$2H^+ + 2e^- \rightarrow H_2, \tag{18}$$

$$CH_3CHO + \cdot OH \rightarrow CH_3CO\cdot + H_2O,^{26)} \tag{19}$$

$$CH_3CO\cdot + \cdot OH \rightarrow CH_3COOH.^{26)} \tag{20}$$

Eq. 17 to Eq. 20 give

$$CH_3CHO + H_2O + 2h^+ + 2e^- \rightarrow CH_3COOH + H_2$$
$$\Delta G^\circ = -25.2\ \text{kJ mol}^{-1}. \tag{21}$$

Although acetic acid was not detected in the present study (its detection limit of about 0.6 μmol), its formation should not be excluded, for CH_4 and CO_2, which are formed from the acid, are evolved as shown in Fig. 3. It seems reasonable to assume that the CH_3COOH required to evolve such a slight amount of CH_4 and CO_2 is only little produced. The H_2 evolved in Eq. 21 is also very low, because of a slight amount of CH_3COOH produced. Such a minor CH_3COOH is almost consumed during the evolution of CH_4 and CO_2. If a slight amount of CH_3COOH exists in the reaction solution, it is almost adsorbed on the surface of the analysis path of the gas chromatograph because of the high adsorptive property of the acid. The water required for Eq. 21 is slightly contained in the reactant C_2H_5OH, and is formed by Eqs. 5, 10, and 15. Actually, H_2O formation was observed.

If CH_4 and CO_2 are evolved by only Eq. 16 when the filter is not used the yield of CH_4 should be equal to that of CO_2. However, as can be seen from Fig. 3, the yield of CH_4 was higher than that of CO_2. That is to say, CH_4 is evolved not

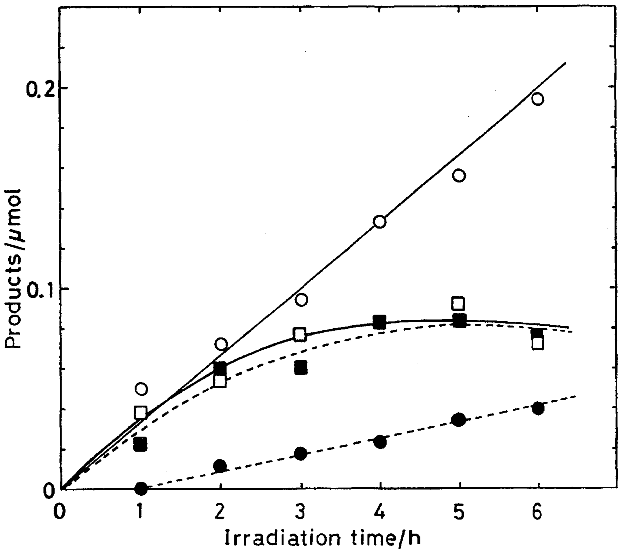

Fig. 3. Formation of CH_4 and CO_2 from a suspension of ethanol (2.0 ml) and TiO_2 (30 mg) under an Ar atmosphere. ○ and ●: CH_4, □ and ■: CO_2, —: without a colored glass filter, ····: with a colored glass filter.

only by Eq. 16, but by an alternate route. The present GC technique can detect the HCHO formed at a yield below 0.2 μmol (the maximum yield observed for CH_4). However, no HCHO was detected. Therefore, CH_4 is not evolved from C_2H_5OH,

$$C_2H_5OH \rightarrow CH_4 + HCHO$$
$$\Delta G^\circ = 22.0\ \mathrm{kJ\,mol^{-1}}. \tag{22}$$

Acetaldehyde is the most abundant product formed from C_2H_5OH, and is the most unstable compound in the products produced from the alcohol. The evolution of CH_4 from CH_3CHO is therefore assumed to be the most possible route,

$$CH_3CHO \rightarrow CH_4 + CO$$
$$\Delta G^\circ = -59.9\ \mathrm{kJ\,mol^{-1}}. \tag{23}$$

Carbon monoxide was not detected. However, even if CO could not be detected, the evolution of CH_4 by the above equation was not completely neglected. The amount of CH_3CHO formed is much less than the reactant C_2H_5OH. If CO is formed at a yield below 0.2 μmol of the maximum yield observed for CH_4, such a small amount of the CO can not be detected, since its detection limit (about 0.6 μmol) is worse than that of CH_4, under the present analytical conditions. Actually, we observed the evolution of CH_4 and CO from CH_3CHO over TiO_2.

Methane decreased appreciably upon the use of a filter. This observation is also explained by decreasing photons due to filtration. The yield of CO_2 was slightly decreased by using the filter. The reason why the drop in the yield of CO_2 due to decreasing photons is lower than that of other products is not understood. However, because CO_2 is the final oxidation product from C_2H_5OH, a slight amount of the gas may be evolved by an unknown route upon using the filter.

We next discuss the relationship between the amount of the C_2H_5OH consumed and the yields of the products from the alcohol. The products from C_2H_5OH are CH_3CHO, acetal, H_2, C_2H_4, CH_4, and CO_2, as described above. However, the yields of H_2, C_2H_4, CH_4, and CO_2 are extremely less than those of CH_3CHO and acetal, and hence little affect the consumption of C_2H_5OH. That is to say, C_2H_5OH is chiefly utilized for the formation of CH_3CHO and acetal. First, we show the consumption of C_2H_5OH without the filter. Because the yield of acetal is 12 μmol after 6 h of irradiation, CH_3CHO of 12 μmol is utilized for the formation of the acetal, as can be seen from Eq. 10. The net amount of the CH_3CHO formed at 6 h of irradiation is not less than at least 21 μmol, which is calculated by the sum of the observed values of 9 μmol and the required values of 12 μmol to produce acetal (12 μmol). Ethanol requires 21 μmol for the formation of CH_3CHO (21 μmol) at Eqs. 4, 5 and needs 24 μmol for that of acetal (12 μmol) at Eq. 10. The C_2H_5OH utilized of 45 μmol is therefore calculated by the sum of both the above values of 21 μmol and 24 μmol. As can be seen Fig. 4, the found decrease for C_2H_5OH at 6 h of irradiation agrees with the calculated C_2H_5OH utilization. When the filter was used, the found decrease for C_2H_5OH at 6 h of irradiation also agreed with the C_2H_5OH utilization calculated in the same way.

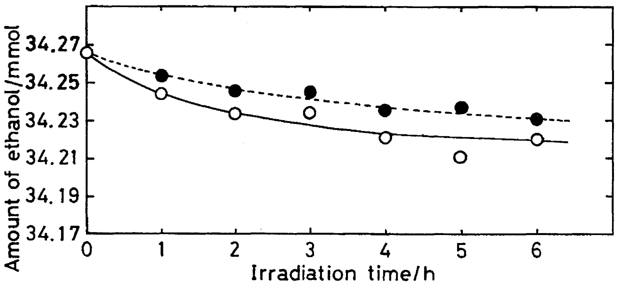

Fig. 4. Amount of ethanol in a suspension of ethanol (2.0 ml) and TiO_2 (30 mg) under an Ar atmosphere. ○: without a colored glass filter, ●: with a colored glass filter.

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