Oxygen Effect on Photocatalytic Reaction of Ethanol over Some Titanium Dioxide Photocatalysts

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The suspensions of four kinds of TiO_2 photocatalysts in ethanol have been studied under ultraviolet light in an atmosphere of Ar, air, or O_2 at 25 °C. The main products were acetaldehyde, acetaldehyde diethyl acetal (acetal), acetic acid, water, ethylene, methane, carbon dioxide, and hydrogen. Acetaldehyde and acetal were abundantly produced in all of the products. The formation of all of the products under O_2 was more efficient than those under Ar and air. The photochemical activity of each TiO_2 is stronger than that of either Ti_2O_3 or TiO.

Photocatalytic H_2 evolution from ethanol over Pt/ TiO_2 catalysts has frequently been reported;[1-6] CH_3CHO,[1,2,4,5] acetal,[2] and acetic acid[1] are major photocatalytic products. However, no instance has yet been reported concerning a quantitative photocatalytic formation on all products from ethanol using various TiO_2 catalysts.

Because the catalytic activity of TiO_2 is presumed to be caused by active oxygen liberated from TiO_2,[7] the activity is decreased by a reduction of the catalyst, itself, due to light illumination;[7] no report, however, has demonstrated the influence of such a decrease in the activity on all products from ethanol, except that regarding the evolution of C_2H_4 and H_2 by the author.[8] To determine the catalytic activity of TiO_2, itself, becomes difficult if Pt is deposited on TiO_2, since the reduction of TiO_2 is depressed by Pt.[9] Therefore, this work was undertaken with only TiO_2, without Pt, and studied in detail regarding effects due to the reactivation of TiO_2 with O_2 on all of the products formed from C_2H_5OH by a comparison of the results from blank tests under Ar, air, or O_2 atmospheres, and that with the TiO_2 under each atmosphere. Furthermore, a comparison was made with that involving TiO_2 as well as Ti_2O_3 or TiO.

Experimental

Photocatalysts. The TiO_2, Ti_2O_3, and TiO used were the same as that described previously.[8] Commercial Ti_2O_3 and TiO used were 99.9%, 300 mesh, Furuuchi Chemical Co., Ltd., respectively.

Ethanol. In the same manner as described in a previous paper,[8] the commercial C_2H_5OH (99.5%, special grade, Katayama Chemical Co., Ltd.) used was purified by distillation after drying over CaO.

Reaction Procedure. The experimental conditions were similar to those published previously.[8] The water tank used was a Riko RH400-10W photochemical reactor. 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 is because the CH_3CHO produced should be kept in the dark while in the liquid-phase as much as possible. A blank test for a mixture of

CH_3CHO (0.2 ml) and H_2O (1.8 ml) or that of CH_3CHO (0.2 ml) and C_2H_5OH (1.8 ml) was carried out under an Ar atmosphere without any catalyst in a similar manner as in a previous study.[10]

Analysis. The analytical conditions were also similar to those run in a previous study.[8] A Shimadzu GC-8A gas chromatograph (activated charcoal, 60—80 mesh) was used for the analysis of gaseous products. All liquid products, except for acetic acid, were analyzed using a Shimadzu GC-4B gas chromatograph (PEG-6000 10%, Flusin P, 30—60 mesh). 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, 140 °C, N_2 carrier, FID). In this experiment, the yields of all products with TiO_2, Ti_2O_3, and TiO include that of a blank test under each atmosphere (Figs. 1,2, and 10).

Results and Discussion

Figures 1 and 2 show the formation of liquid products and that of gaseous products from ethanol versus the illumination time observed for a blank test under an Ar or air atmosphere, respectively. Because CH_3CHO and H_2 are produced during the initial illumination, the first reaction of ethanol proceeds as follows:[1]

$$C_2H_5OH \xrightarrow{h\nu} CH_3CHO + H_2 \quad \Delta G° = 41.0 \text{ kJ mol}^{-1}. \quad (1)$$
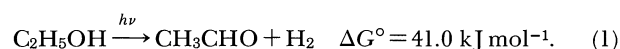
This result is particularly important in view of the fact that ethanol fails to undergo any reaction; this is because of its absorption maximum at 174 nm[11] under UV light, since Pyrex glass does not pass UV light below about 230 nm. The cause of the reaction described in Eq. 1 is most likely to be due to slight substances having photosensitive action dissolved in ethanol from the natural rubber liner; natural rubber usually contains small amounts of other additive impurities. Once CH_3CHO forms, it serves as a sensitizer, since it has an absorption maximum at 293 nm[12] in its ultraviolet spectrum, and Pyrex glass passes about 40% of the UV light at a wavelength of 290 nm. Accordingly, some of the products shown in Figs. 1 and 2 were slightly produced without TiO_2. Acetal and CH_3COOH were not detected at for illumi-
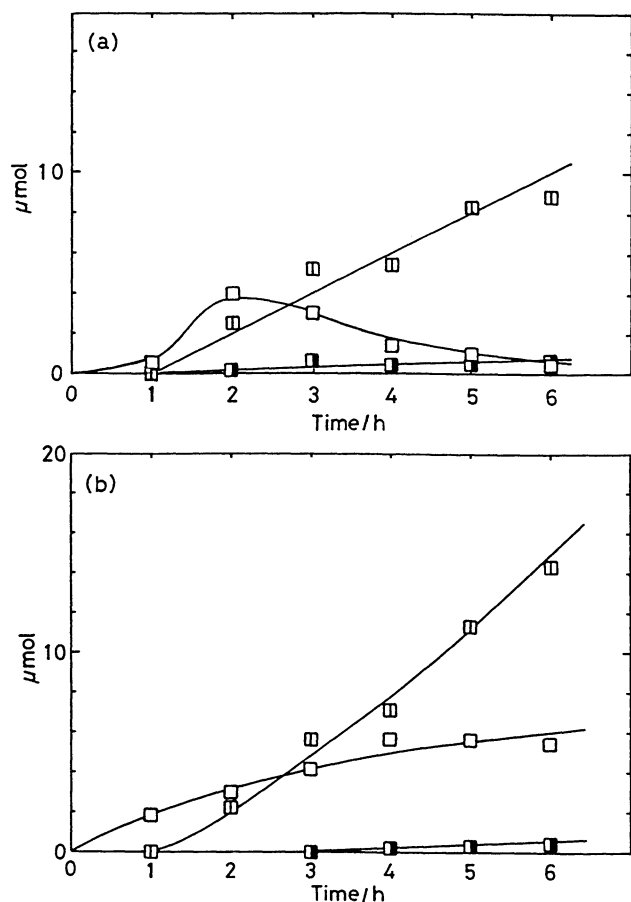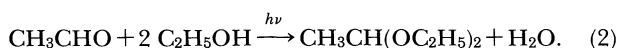
Fig. 1. Formation of liquid products from 2.0 ml ethanol vs. illumination time for a blank test without any TiO₂ under Ar (a) or air (b) atmosphere. □: acetaldehyde, ▥: acetaldehyde diethyl acetal (acetal), ◨: acetic acid.
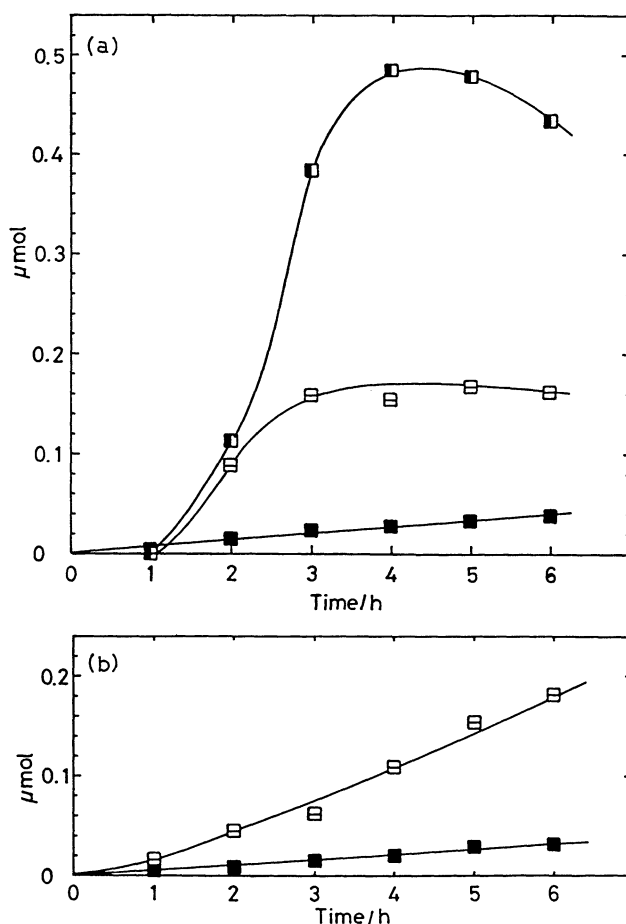

Fig. 2. Evolution of gaseous products from 2.0 ml ethanol vs. illumination time for a blank test without any TiO₂ under Ar (a) or air (b) atmosphere. □: CH₄, ◨: CO₂, ■: H₂.

nation times less than 1 h, and therefore appear to be formed in the following way:

$$CH_3CHO + 2 \; C_2H_5OH \xrightarrow{h\nu} CH_3CH(OC_2H_5)_2 + H_2O. \quad (2)$$

Actually, this reaction was confirmed by the formation of acetal and H_2O from a mixture of CH_3CHO (0.2 ml) and C_2H_2OH (1.8 ml) under an Ar atmosphere without TiO_2. Acetic acid is formed as proposed by Sakata and Kawai,[1]

$$CH_3CHO + H_2O \xrightarrow{h\nu} CH_3COOH + H_2$$
$$\Delta G^\circ = -18.9 \text{ kJ mol}^{-1}. \quad (3)$$

The formation of CH_3COOH and H_2 was also observed in a mixture of CH_3CHO (0.2 ml) and H_2O (1.8 ml) under Ar. In addition, CH_4 and CO_2 from Eq. 4, shown later, were evolved. The H_2O in Eq. 3 is contained as a small amount of impurity in ethanol and is provided by Eq. 2 as well as by the oxidation of C_2H_5OH by O_2 under an air atmosphere.[8] Actually, H_2O formation under air was more than that under an Ar atmosphere.

No evolution of CH_4 and CO_2 was detected for illumination times less than 1 h under Ar. This is because the decomposition of CH_3COOH gives an evolution of CH_4 and CO_2, as reported by Kraeutler and Bard,[13] and no CH_3COOH was formed during the initial stage.

$$CH_3COOH \xrightarrow{h\nu} CH_4 + CO_2 \quad \Delta G^\circ = -55.8 \text{ kJ mol}^{-1}. \quad (4)$$
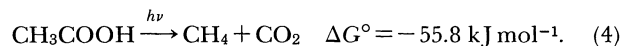
By the way, in spite of the formation of CH_3COOH and CO_2 under air, no CH_4 was detected. One possible reason for no CH_4 evolution involves the oxidation of CH_4 by O_2 in air.

Figure 3 shows the formation of CH_3CHO from ethanol versus the illumination time observed for four TiO_2 catalysts under an atmosphere of Ar and that of air. Because of the higher yield with each TiO_2, compared to the yield of the blank test, all of the TiO_2 contributes to the formation of CH_3CHO. Acetaldehyde is also formed by the reduction of TiO_2, itself, as shown in Eq. 5 for the following reason. Buss and co-workers proposed the formation of Ti_2O_3 through a color change of the illuminated TiO_2 in normal
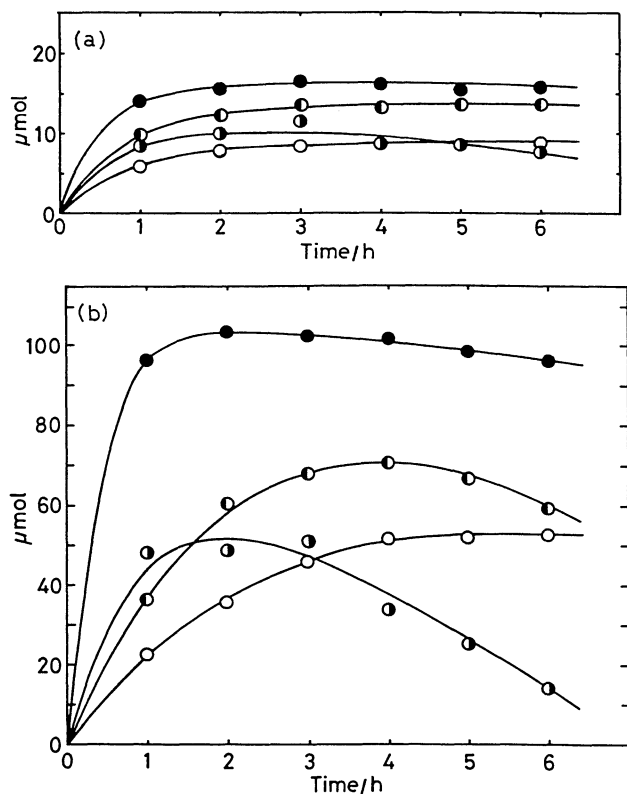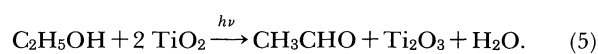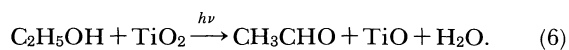
Fig. 3. Formation of acetaldehyde vs. illumination time for suspensions of 30 mg TiO₂ in 2.0 ml ethanol under Ar (a) or air (b) atmosphere. O: anatase (Aldrich), ◑: rutile (Aldrich), ◐: rutile (Furuuchi), ●: P-25 (Nippon Aerosil).

Fig. 4. Formation of products vs. illumination time for suspension of 30 mg Ti₂O₃ in 2.0 ml ethanol under Ar (a) or air (b) atmosphere. □: acetaldehyde, ⊟ CO₂, ■: H₂.

Fig. 5. Formation of products vs. illumination time for suspension of 30 mg TiO in 2.0 ml ethanol under Ar (a) or air (b) atmosphere. □: acetaldehyde, ▣: acetal, ▯: CH₄, ⊟: CO₂, ■: H₂.

primary alcohols.[14] Nishimotol et al. demonstrated the cause for the color change by which Ti₂O₃ is formed by a reduction of TiO₂ with 2-propanol.[9] Judging from these two reports, the color change of illuminated TiO₂ in the present work is considered to be caused by a partial formation of Ti₂O₃ due to the reduction of TiO₂ with ethanol,

$$C_2H_5OH + 2\ TiO_2 \xrightarrow{h\nu} CH_3CHO + Ti_2O_3 + H_2O. \quad (5)$$

The molar quantities of TiO₂ required to react with 2.0 ml (343×10^2 μmol) of ethanol are 686×10^2 μmol, as can be seen from Eq. 5. However, 30 mg (375 μmol) of TiO₂ is about 1/200 of the value of μmol required to react with 2.0 ml of ethanol. Therefore, the TiO₂ may be further reduced with a large excess of the ethanol,

$$C_2H_5OH + TiO_2 \xrightarrow{h\nu} CH_3CHO + TiO + H_2O. \quad (6)$$

If only gaseous O₂ in the reaction tube contributed to the formation for CH₃CHO, the ratio of CH₃CHO formation under Ar to that under air in a blank test should be the same as that with TiO₂. However, the formation of CH₃CHO with most TiO₂ catalysts under air is above about 5-times that under Ar, while its formation in a blank test under air is approxi-
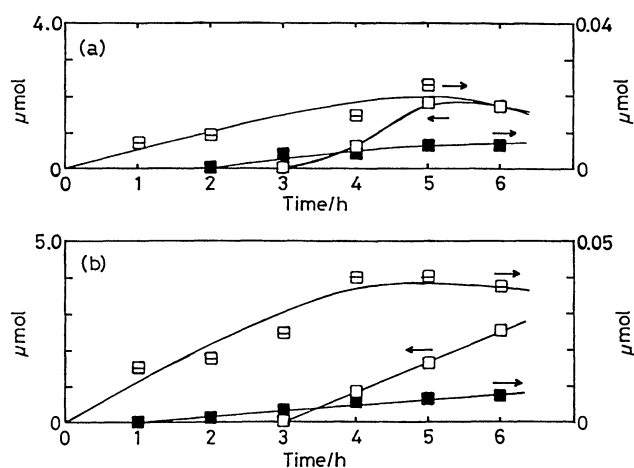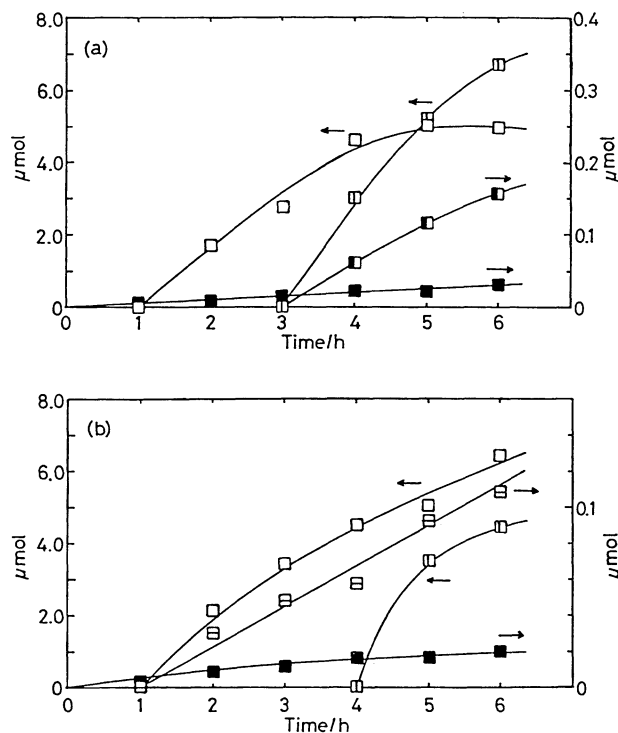
mately twice that under Ar. Such a difference between the ratio with the TiO₂ and that in the blank test is remarkably observed for other products, as shown later, since the yields of the other products under Ar in the blank test are roughly the same as those under air, in contrast to the larger difference in the yields with the TiO₂ than the result for CH₃CHO. Consequently, the active O₂ from the reoxidized

TiO$_2$[7] by O$_2$ in air seems to be the reason for the higher yield of CH$_3$CHO under air than that under Ar. If this assumption were correct, the color change[9,14] due to the reduction of TiO$_2$ observed under air should be much less than that under Ar; further, O$_2$ in the reaction tube must be decreased, and water must be formed. In fact, these three observations were obtained. To make sure of this estimate, we tried to produce CH$_3$CHO with Ti$_2$O$_3$ or TiO corresponding to the reduction product of TiO$_2$; these two catalysts gave much fewer products, as shown in Figs. 4 and 5, respectively. Accordingly, the retarding photochemical reduction of TiO$_2$ under an air atmosphere led to much CH$_3$CHO formation.

Figure 6 shows the formation of acetal. Under Ar, in spite of the higher yield of CH$_3$CHO with P-25 and rutile (Furuuchi), compared to the rutile (Aldrich), these two TiO$_2$ gave no acetal. Although there was no large difference between the yield of CH$_3$CHO with rutile (Aldrich) and that with anatase, the anatase yielded no acetal. It is therefore evident that these three TiO$_2$ of P-25, rutile (Furuuchi), and anatase did not catalyze the formation of acetal under Ar.

In the case of an air atmosphere, all of the TiO$_2$, except for anatase, gave more acetal than that under Ar. That only anatase gave no acetal is interesting, since this TiO$_2$ produces CH$_3$CHO.

Figure 7 shows the formation of CH$_3$COOH. The water in Eq. 3 required to produce CH$_3$COOH is further supplied from Eqs. 5 and 6, and the evolution of C$_2$H$_4$ from C$_2$H$_5$OH,[8,10] besides being available from only a small amount of H$_2$O in ethanol and H$_2$O

from Eq. 2.

In spite of no large difference in the yield of CH$_3$CHO (Fig. 3, under Ar), no CH$_3$COOH can be detected on both rutiles (Aldrich and Furuuchi) and P-25 in Ar. However, it seems reasonable to assume that these three TiO$_2$ may also produce in practice CH$_3$COOH, due to CH$_4$ and CO$_2$ formation in Eq. 4 from the CH$_3$COOH formed with all of the TiO$_2$ tested (as is shown later). Each yield of their CH$_3$COOH, however, seems to be much less than the yield with anatase, and such a minor CH$_3$COOH is almost consumed during the evolution of CH$_4$ and CO$_2$, accordingly to Eq. 4. If a slight amount of CH$_3$COOH exists in the reaction solution after decomposition to CH$_4$ and CO$_2$, 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 more rapid decomposition rate of CH$_3$COOH with both rutiles and P-25 than anatase may have also been a cause for no detection of the acid.

All of the TiO$_2$ in an air atmosphere catalyzes the formation of CH$_3$COOH and gives much more CH$_3$COOH than that under Ar. Anatase did not give as much CH$_3$CHO as that shown in Fig. 3, but never-

Fig. 7. Formation of acetic acid vs. illumination time for suspensions of 30 mg TiO$_2$ in 2.0 ml ethanol under Ar (a) or air (b) atmosphere. O: anatase (Aldrich), ◑: rutile (Aldrich), ◐: rutile (Furuuchi), ●: P-25 (Nippon Aerosil).
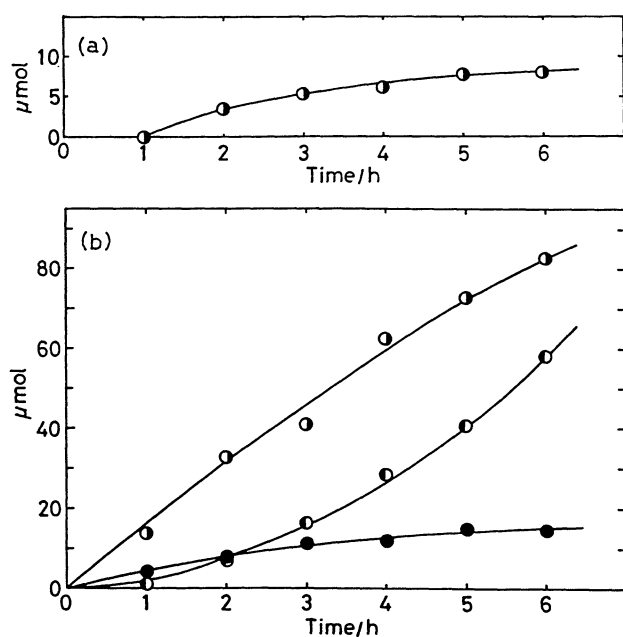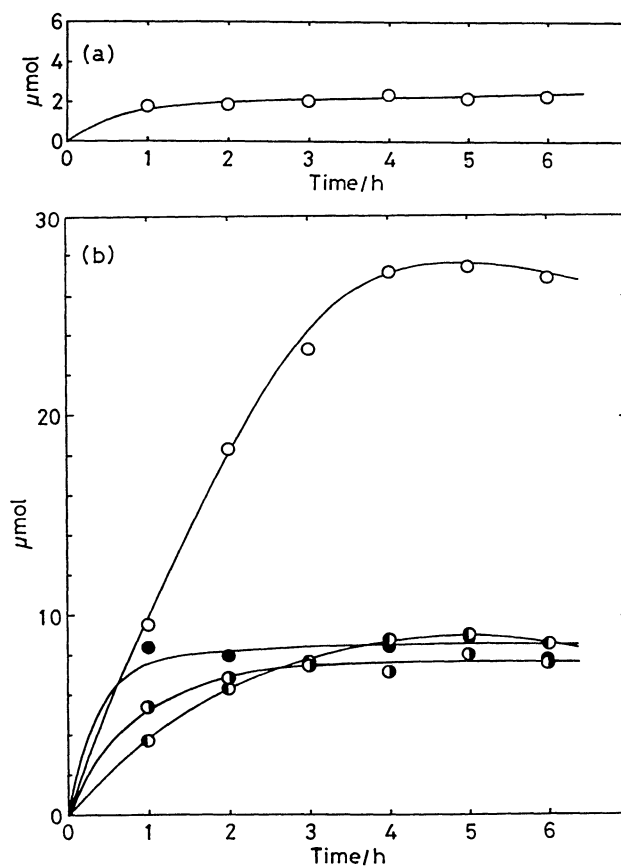

Fig. 6. Formation of acetal vs. illumination time for suspensions of 30 mg TiO$_2$ in 2.0 ml ethanol under Ar (a) or air (b) atmosphere.◑: rutile (Aldrich), ◐: rutile (Furuuchi), ●: P-25 (Nippon Aerosil).

theless showed a much higher CH_3COOH yield than did the other TiO_2 catalysts. This is because only anatase did not give acetal (Fig. 6), which is produced from CH_3CHO, as shown in Eq. 2. That is to say, because CH_3CHO with anatase produced CH_3COOH without being used up in the formation of acetal, the anatase could give the greatest CH_3COOH yield.

Figure 8 shows the evolution of CH_4. In the case of an Ar atmosphere, since no evolution of CH_4 took place in the blank test during the initial time, all of the TiO_2 catalyzed evolving CH_4 at that time. However, since the yield of CH_4 was much less than that in the blank test, oxidation of the CH_4 by the O_2 released from TiO_2 seems to be the reason for this result.

All of the TiO_2 under an air atmosphere catalyzed the evolution of CH_4, since no CH_4 evolved in a blank

test under air. The result that CH_4 evolution under air is more than that under Ar is consistent with a similar data observed regarding CH_3COOH formation, since CH_4 evolves from CH_3COOH.

Figure 9 shows the evolution of CO_2. All of the TiO_2 gives much more CO_2 under air than that under an Ar atmosphere, because CH_3COOH formation under air is much higher than that under Ar.

Because the evolution of H_2 and C_2H_2 under Ar and air had been previously reported,[8,10] it was omitted.

As described above, air has been found to be effective for the formation of all products; to prove such an effect, further experiments were performed under an O_2 atmosphere.

Figure 10 shows the formation of products from ethanol observed for a blank test under an O_2 atmosphere. Although trace amounts of CH_3COOH and CH_4 were detected, no C_2H_4 evolved. Only the yield of CO_2 was more than that under air (Fig. 2).

Figure 11 shows the formation of liquid products from ethanol versus the illumination time observed for the TiO_2 (rutile, Furuuchi) under an atmosphere of O_2. All of the products were formed in greater quantities than those under air.
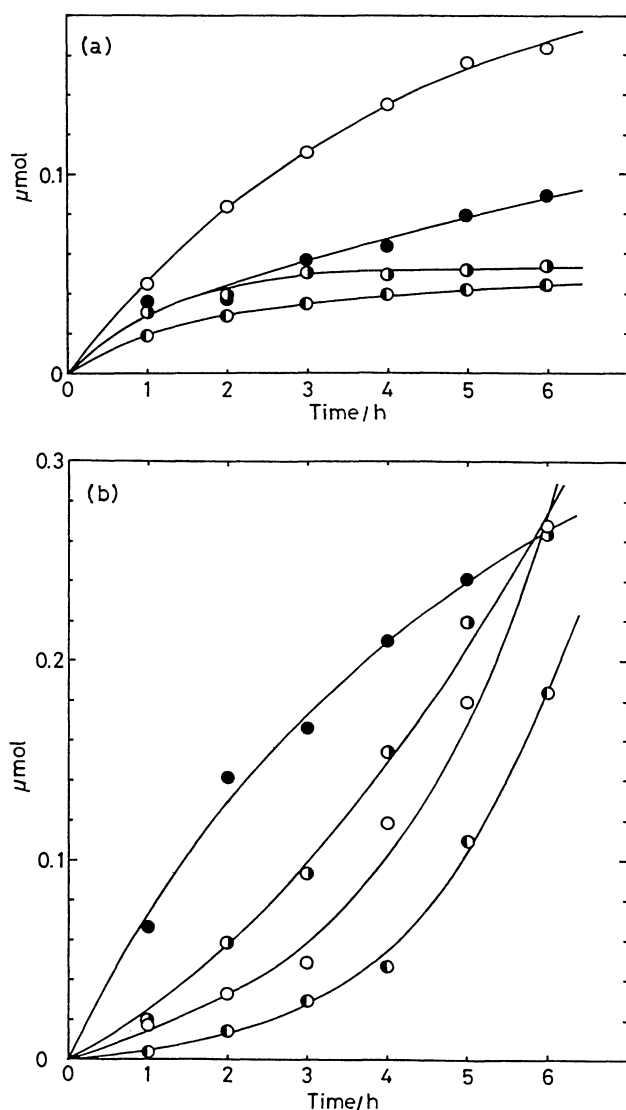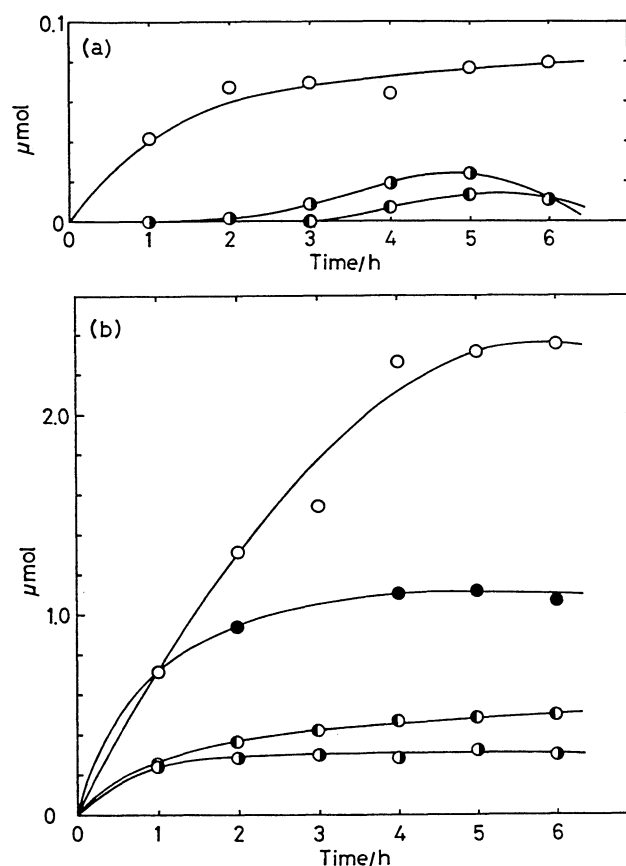

Fig. 8.   Evolution of CH_4 vs. illumination time for suspensions of 30 mg TiO_2 in 2.0 ml ethanol under Ar (a) or air (b) atmosphere.   O: anatase (Aldrich), ◑: rutile (Aldrich), ◐: rutile (Furuuchi), ●: P-25 (Nippon Aerosil).

Fig. 9.   Evolution of CO_2 vs. illumination time for suspensions of 30 mg TiO_2 in 2.0 ml ethanol under Ar (a) or air (b) atmosphere.   O: anatase (Aldrich), ◑: rutile (Aldrich), ◐: rutile (Furuuchi), ●: P-25 (Nippon Aerosil).
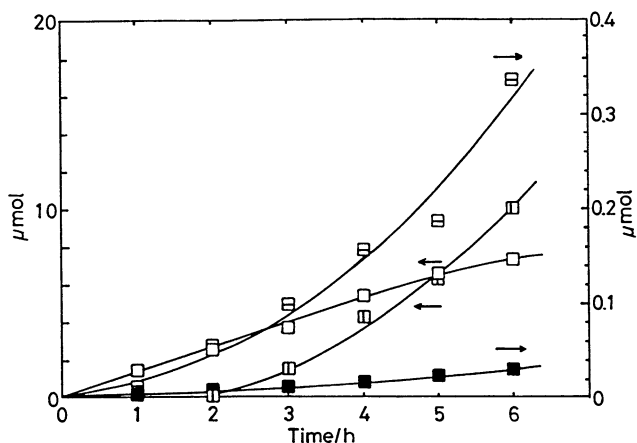
Fig. 10.   Formation of products from 2.0 ml ethanol vs. illumination time for a blank test without any TiO2 under O2 atmosphere.   □: acetaldehyde, ▥: acetaldehyde diethyl acetal (acetal), ⊟: CO2, ■: H2.

Fig. 12.   Evolution of gaseous products vs. illumination time for suspension of 30 mg TiO2 (rutile, Furuuchi) in 2.0 ml ethanol under O2.   ⊞: C2H4, ◨: CH4, ⊟: CO2, ■: H2.
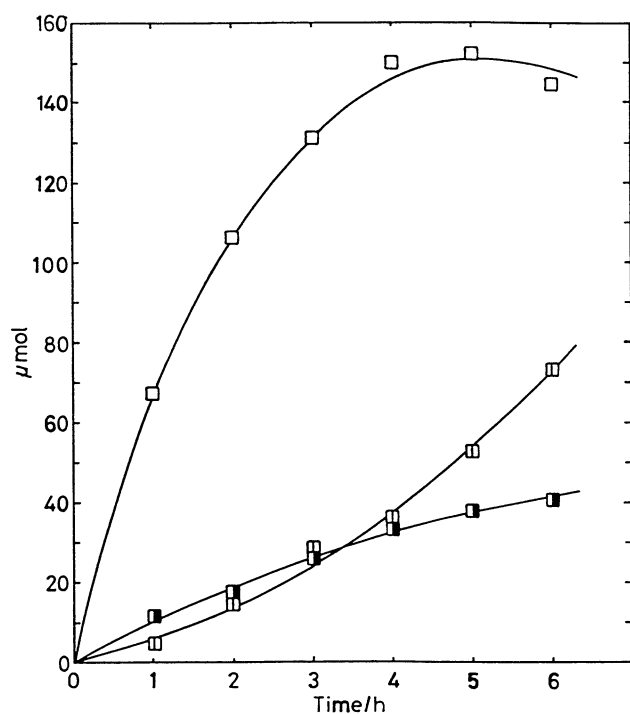

Fig. 11.   Formation of liquid products vs. illumination time for suspension of 30 mg TiO2 (rutile, Furuuchi) in 2.0 ml ethanol under O2.   □: acetaldehyde, ▥: acetaldehyde diethyl acetal (acetal), ◨: acetic acid.

Figure 12 shows the formation of gaseous products with TiO2 (rutile, Furuuchi) under O2. All of the gaseous products, except for CH4, were formed in greater quantities than those under an air atmosphere. One possible reason why only CH4 evolution is less than that under air is as given below. In a blank test, no CH4 was formed under O2 and air, although it was evolved under Ar. Judging from
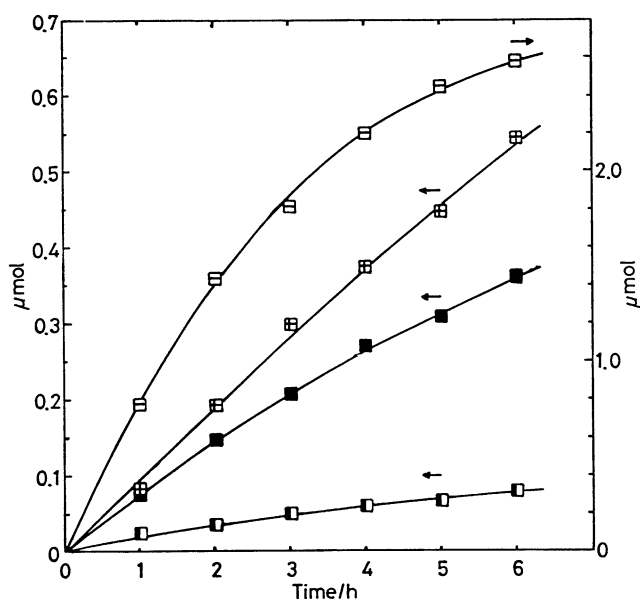
these results, even if CH4 evolved more than that under air, it was further oxidized by excess O2 in the reaction tube. The fact that the CO2 yield was about 5-times that under air supports this assumption.

The yield of C2H4 vs. the illumination time is approximately linear, while under air it gave a downward curvature.[8] The reason for such a high activity of TiO2 is a smaller reduction of part of the TiO2 than that under air. Actually, no color change[9,14] due to a reduction of TiO2 was observed, in contrast to the result under air.

The differences among the yields regarding products with TiO2 under Ar, air, and O2 was much larger than that in blank tests under these three atmospheres; the yields with TiO2 increased in the order Ar < air < O2 atmosphere. Consequently, it has become apparent that active O2 from reoxidized TiO2 by O2 in the reaction tube has a considerably greater effect on the photolysis of ethanol with TiO2 than does gaseous O2 present in the reaction tube.

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