

Photocatalytic partial oxidation of methylpyridine isomers on TiO₂ particles under an anaerobic condition

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Abstract

Photocatalytic oxidation of methylpyridine isomers (2-methylpyridine, 3-methylpyridine, and 4-methylpyridine) was investigated in a mixed solution of acetonitrile and water or acetonitrile using various kinds of TiO₂ powders as photocatalysts. The main products from methylpyridine isomers were pyridinecarboxaldehyde isomers (2-pyridinecarboxaldehyde, 3-pyridinecarboxaldehyde, and 4-pyridinecarboxaldehyde). Rutile large TiO₂ particles showed the highest level of activity for oxidation of 2-methylpyridine probably because band bending was necessary for the oxidation of 2-methylpyridine. On the other hand, a fine particle having an anatase or rutile phase showed a higher level of activity than large TiO₂ particles for oxidation of 3-methylpyridine. A rutile fine particle showed the highest level of activity for the reaction. It was found that pure rutile or pure anatase particles were inactive for oxidation of 4-methylpyridine. If the particles are not extremely small, pure rutile and pure anatase powders show fairly high levels of activity, and those containing both anatase and rutile phases show the highest level of activity. The activity of pure rutile particles was also enhanced by physically mixing them with a small amount of small anatase particles, which were inactive for this reaction. These results can be explained by the synergism between rutile and anatase particles. All of these reactions effectively proceeded even under anaerobic conditions. Photocatalytic reduction of methylpyridine isomers concomitantly proceeded on TiO₂ particles under the conditions used. These results suggest that the activities of TiO₂ photocatalysts for oxidation of methylpyridine isomers are dominated by the oxidation potential of alkylpyridine and band bending of TiO₂ particles.

1. Introduction

Titanium dioxide (TiO₂)-mediated heterogeneous photocatalysis has attracted great attention because of its potential applications to decomposition of pollutants in water and air [1–5]. TiO₂ and some other semiconductor photocatalysts have also been extensively studied for the purpose of solar energy conversion [6–11]. Organic synthesis is another active research field of TiO₂ photocatalysts [12–20]. In many applications, anatase TiO₂ powders consisting of particles with large surface areas are used as photocatalysts. These powders are advantageous for adsorption of isomers included in the reaction system at low concentrations. Typical compounds that efficiently react on fine anatase powders are phenols [19] and olefins [16]. In contrast to these compounds, oxidation of water efficiently proceeds on large rutile TiO₂ particles [4, 5, 9]. It has been shown from photoelectrochemistry of TiO₂ electrodes that band bending is necessary for oxidation of water. Thus, it is thought that TiO₂ photocatalyst particles used for

this reaction must be large enough to develop a space charge near the surface [6].

We report here that partial oxidation of methylpyridine isomers to generate pyridinecarboxaldehyde isomers effectively proceeds on TiO₂ particles under deep UV irradiation and anaerobic conditions. The activity of the TiO₂ photocatalyst for oxidation of methylpyridine isomers varies depending on the position of the methyl group of pyridine. The mechanism of the reaction is also discussed.

2. Experimental

2.1. Materials and instruments

Various kinds of titanium dioxide (TiO₂) powder having anatase and rutile crystal structures were obtained from the Catalysis Society of Japan (TIO-3, TIO-5), Ishihara Sangyo (ST-01, ST-21, ST-41, and CR-EL), TAYCA

Corporation (AMT-100, AMT-600, and MT-150A) and Japan Aerosil (P-25). The contents of anatase and the surface areas of these powders were as follows: ST-01: 100%, 320.5 m² g⁻¹; ST-21: 100%, 56.1 m² g⁻¹; ST-41: 100%, 8.2 m² g⁻¹; CR-EL: 0%, 7.1 m² g⁻¹; AMT-100: 100%, 290.0 m² g⁻¹; AMT-600: 100%, 59.0 m² g⁻¹; MT-150A: 0%, 81.5 m² g⁻¹; TIO-3: 0%, 48.1 m² g⁻¹; TIO-5: 9%, 2.5 m² g⁻¹; P-25: 83.5%, 49.2 m² g⁻¹. 2-Methylpyridine, 3-methylpyridine, and 4-methylpyridine were obtained from Wako Pure Chemical Industry as guaranteed reagents and were used without further purification. 2-Pyridinecarboxaldehyde, 3-pyridinecarboxaldehyde, and 4-pyridinecarboxaldehyde were purchased from Sigma Aldrich Japan Company as guaranteed reagents and were used without further purification. Other chemicals were obtained from commercial sources as guaranteed reagents and used without further purification. The contents of rutile and anatase phases in TiO₂ powders were determined by X-ray diffraction spectroscopy (XRD, Philips, X'Pert-MRD). The morphology of TiO₂ powders was examined by using a scanning electron microscope (SEM, Hitachi S-5000). The surface area of the powder was determined by using a surface area analyzer (Micromeritics, FlowSorb II 2300).

2.2. Photocatalytic reaction and analysis of the products

Photocatalytic reactions were typically carried out in Pyrex glass tubes filled with a mixture of acetonitrile (3.6 g) and water (0.4 g) or pure acetonitrile (4.0 g). A methylpyridine compound (2-methylpyridine, 3-methylpyridine, or 4-methylpyridine) (0.5 g) and TiO₂ powder (0.05 g) were added to the solution. TiO₂ particles were suspended in the solution by sonication for 1 min before the reaction. Before photoirradiation, the solution was bubbled with oxygen at a rate of 1.5 ml min⁻¹ for 15 min, and the glass tube was sealed by a septum. A 500 W super pressure mercury lamp (Wacom, BMO-500DY) was used as a light source, and a UV35filter (Kenko Co.) was used to remove deep UV light ($\lambda < 350$ nm) and prevent direct photoexcitation of methylpyridine isomers. The light intensity was controlled using fine stainless-steel meshes as neutral density filters.

After photoirradiation for certain time periods, the solutions were analyzed with high-performance liquid chromatographs (HPLC, GL Science UV620 and Hitachi D-7500), equipped with an ODS-80Ts column, using a mixture of water (2.5 mM K₂HPO₄, 2.5 mM KH₂PO₄ and 0.1 M NaClO₄) and methanol (9:1) as the eluent. The reaction products were identified by coinjecting corresponding authentic samples. Each solution was also analyzed with a capillary gas chromatograph (Shimadzu GC-14B) equipped with a DB-1 capillary column.

2.3. Oxidation of 2-methylpyridine using Fenton's reagent [21]

Photocatalytic reactions were typically carried out in Pyrex glass tubes filled with a mixture of H₂O₂ (0.097 M,

5.0 ml) and FeCl₂·4H₂O (0.192 g). An acetonitrile solution of 2-methylpyridine (0.0097 M, 50.0 ml) was added to the solution. The solution was magnetically stirred for 5 min. After the reaction, an NaOH aqueous solution (0.58 M, 10.0 ml) was added to the reaction solution to precipitate Fe(OH)₃. The solution was centrifuged followed by filtration. The resulting solution was analyzed by HPLC, the conditions such as the eluent and column used, being the same those described in the previous section.

2.4. Origin of oxygen for oxidation of methylpyridine isomers using TiO₂ photocatalysts

In order to identify the origin of oxygen introduced into pyridinecarboxaldehyde isomers as an aldehyde group, water containing isotope oxygen (¹⁸O) was added to the reaction solution. After photoirradiation, products were analyzed by means of GC-MS. The experimental procedure is as follows.

Photocatalytic reactions were typically carried out in Pyrex glass tubes filled with a mixture of acetonitrile (3.6 g) and H₂¹⁸O (0.4 g). Methylpyridine isomers (2-methylpyridine, 3-methylpyridine or 4-methylpyridine) (0.5 g) and TiO₂ powder (0.05 g) were added to the solution. Before photoirradiation, the solution was bubbled with oxygen at a rate of 1.5 ml min⁻¹ for 15 min, and the glass tube was sealed by a septum. A 500 W super pressure mercury lamp (Wacom, BMO-500DY) with a UV35filter (Kenko Co.) was used as a light source.

After photoirradiation for certain time periods, the solutions were analyzed with a GC-MS spectrometer (JEOL JMS-DX303HF) equipped with a DB-1 column. The molecular weight was determined with a GC-MS spectrometer (JEOL JMS-DX303HF) equipped with a DB-1 column.

2.5. Role of oxygen in partial oxidation of methylpyridine isomers

In order to elucidate the role of oxygen in the reaction, photocatalytic reactions were carried out under reduced pressure or under a nitrogen atmosphere. Under a nitrogen atmosphere, the solution was bubbled with nitrogen at a rate of 1.5 ml min⁻¹ for 15 min, and the glass tube was sealed by a septum. In the case of the reaction under reduced pressure, oxygen dissolved in the solution was completely removed using freeze-pump-and-thaw cycles. Other conditions such as the concentration of methylpyridine isomers and amount of TiO₂ used are the same as those in the case of photocatalytic oxidations of methylpyridine isomers under an aerobic condition.

2.6. Preparation of the TiO₂ powders containing rutile and anatase phases

TiO₂ powders containing both anatase and rutile phases were prepared by physical mixing of a rutile powder

with an anatase powder at different ratios. A rutile powder (CR-EL) was used as a standard material of rutile particles. For mixing this pure rutile powder with an anatase (ST-01) powder, the powders were added to acetonitrile at certain ratios, and the mixtures were sonicated for 30 min.

3. Results and discussion

3.1. Photocatalytic reaction of methylpyridine isomers on TiO_2 photocatalysts

3.1.1. Photooxidation of 2-methylpyridine using TiO_2 powders as photocatalysts

The rate of production of 2-pyridinecarboxaldehyde depended on the TiO_2 powder used as the photocatalyst, but 2-pyridinecarboxaldehyde was always the main product using any kind of TiO_2 powder. Among the TiO_2 powders we investigated, extremely large TiO_2 particles (CR-EL) having a pure rutile phase showed the highest level of photocatalytic activity for the production of 2-pyridinecarboxaldehyde as shown in Figure 1. However, very small anatase particles (ST-01 and AMT-100), which are commonly used as photocatalysts, showed very low activity levels in this reaction. These results indicate that band bending is necessary to improve photocatalytic activity. Moreover, the activity of rutile TiO_2 was much greater than that of anatase TiO_2 if the sizes of these particles were nearly the same. These results are in accordance with the results of photooxidation of water reported in our previous paper [6].

3.1.2. Photooxidation of 3-methylpyridine using TiO_2 powders as photocatalysts

The main product of photooxidation of 3-methylpyridine was confirmed to be 3-pyridinecarboxaldehyde. Among the TiO_2 powders we investigated, a pure rutile

powder (MT-150A) having a large surface area showed the highest level of photocatalytic activity as shown in Figure 2. Similarly, pure anatase fine particles such as ST-01 and AMT-100 having large surface areas showed fairly high levels of activity. These results suggest that the adsorbivity of 3-methylpyridine on the surface of TiO_2 and oxidation powder of TiO_2 is the most important factor for improving photocatalytic activity.

3.1.3. Photooxidation of 4-methylpyridine using TiO_2 powders as photocatalysts

The rate of production of 4-pyridinecarboxaldehyde depended on the TiO_2 powder used, but 4-pyridinecarboxaldehyde was always the main product using any kind of TiO_2 powder as shown in Figure 3. Among the TiO_2 powders we investigated, a powder (P-25) that contains both anatase and rutile particles [22] showed the highest levels of photocatalytic activity for the production of 4-pyridinecarboxaldehyde. Pure anatase particles showed fairly high levels of activity if their sizes were not extremely small. Pure rutile particles of relatively large sizes also showed a fairly high level of activity, though the level was lower than that of pure anatase particles of nearly the same size. However, very small anatase particles (ST-01 and AMT-100), which are commonly used as the photocatalysts, showed very low levels of activity in this reaction.

3.2. Effect of water for oxidation of methylpyridine isomers using anatase TiO_2 powders

In order to clarify the role of water for oxidation of methylpyridine isomers, the photocatalytic reactions carried out in a mixture solvent of water and acetonitrile. Photocatalytic activities of anatase TiO_2 powders for oxidation of methylpyridine isomers were greatly

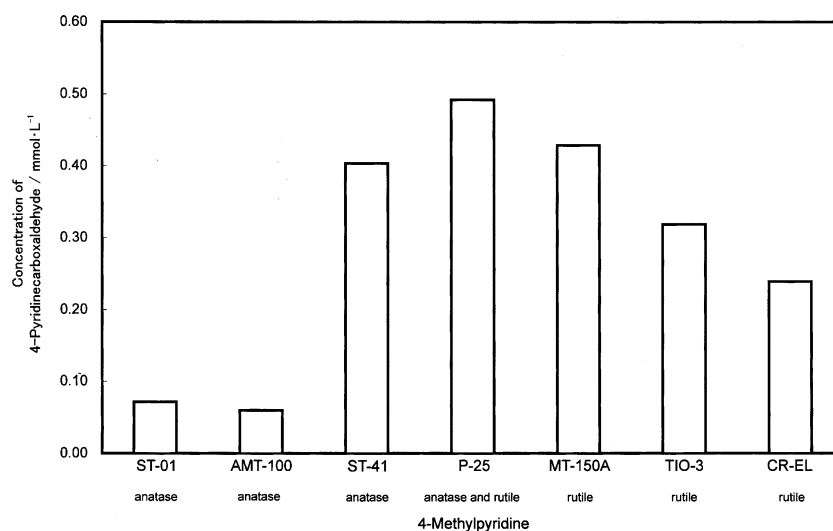


Fig. 1. Amounts of 2-pyridinecarboxaldehyde after photoirradiation for 1 h using several TiO_2 powders. The reaction was carried out in a CH_3CN (4.0 g) containing 2-methylpyridine (0.5 g) and TiO_2 powders (50 mg) as photocatalysts. A light beam was passed through a glass filter (UV-35) to remove deep UV light ($\lambda < 340$ nm). The experimental conditions are described in detail in Section 2.

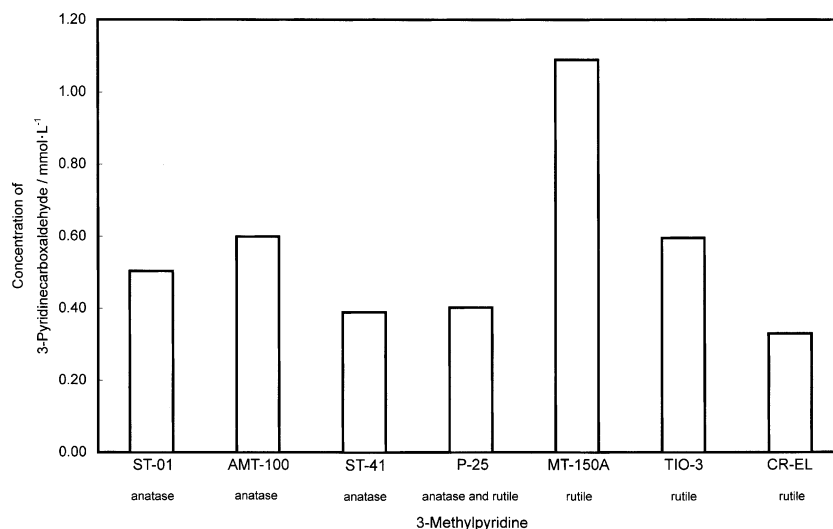


Fig. 2. Amounts of 3-pyridinecarboxaldehyde generated from 3-methylpyridine after photoirradiation for 1 h using several TiO₂ powders. Experimental conditions are the same as those used in the experiment for which results are shown in Figure 1.

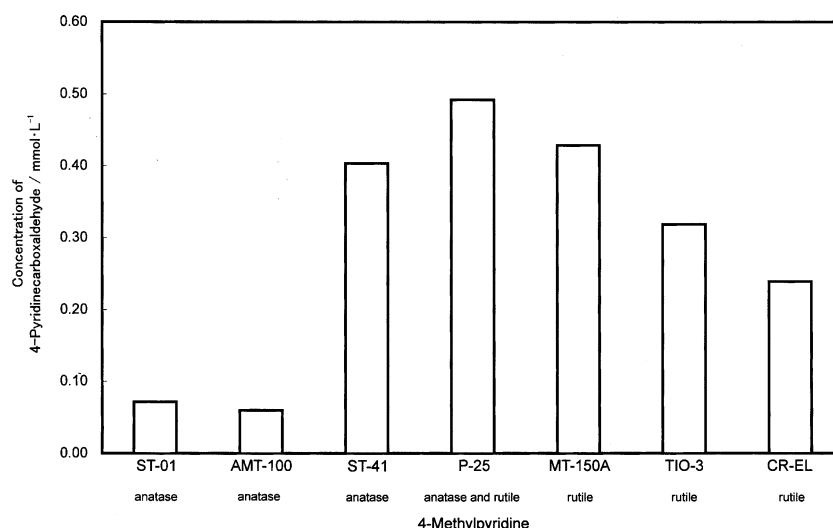


Fig. 3. Amounts of 4-pyridinecarboxaldehyde generated from 4-methylpyridine after photoirradiation for 1 h using several TiO₂ powders. Experimental conditions are the same as those used in the experiment for which results are shown in Figure 1.

improved by addition of water to the acetonitrile solution as shown in Figure 4. These results suggest that water is included in the reaction scheme for oxidation of methylpyridine isomers to generate pyridinecarboxaldehyde isomers. In contrast to the results using anatase powders as photocatalysts, photocatalytic activities of a pure rutile TiO₂ powder did not change or slightly decreased because oxidation of water is thought to compete with oxidation of methylpyridine isomers on rutile TiO₂ particles. On the other hand, anatase TiO₂ particles do not have enough power for oxidation of water [6].

3.3. Origin of oxygen of an aldehyde group of pyridinecarboxaldehyde as a result of oxidation of methylpyridine isomers using TiO₂ photocatalysts

In order to clarify the contribution of free OH radicals as an oxygen source to the oxidation of 3-methylpyridine,

we applied Fenton reagents to the reactions, which supplied free OH radicals. After reaction for 5 min, the solution was analyzed by GC and HPLC. However, no product such as 3-pyridinecarboxaldehyde was observed as shown in Figure 5. This result suggests that the free OH radicals were not active species to produce 3-pyridinecarboxaldehyde.

We also investigated the origin of oxygen that was introduced into the products of photocatalytic oxidation of 3-methylpyridine as an aldehyde group. In order to identify the origin of oxygen introduced into 3-pyridinecarboxaldehyde as an aldehyde group, water containing isotope oxygen (¹⁸O) was added to the reaction solution. By the addition of water containing isotope oxygen, products containing isotope oxygen were obtained. Molecular weight of pyridinecarboxaldehyde isomers generated photocatalytically is 110 (M + 3). This result indicates that oxygen of water was introduced into an aldehyde group of 3-pyridinecarboxaldehyde.

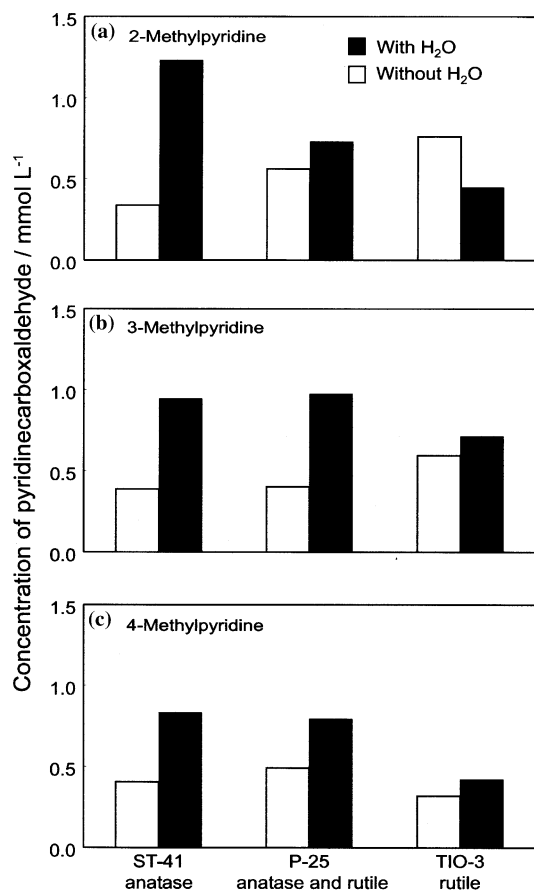


Fig. 4. Amounts of pyridinecarboxaldehyde isomers generated from methylpyridine isomers after photoirradiation for 1 h using several TiO₂ powders. The reaction was carried out in a mixed solvent of CH₃CN (3.6 g) and H₂O (0.4 g) containing methylpyridine isomers (0.5 g) and TiO₂ powders (0.05 g) as photocatalysts. A light beam was passed through a glass filter (UV-35) to remove deep UV light ($\lambda < 340$ nm). The experimental conditions are described in detail in Section 2.

3.4. Role of oxygen in oxidation of methylpyridine isomers

In order to elucidate the reduction by photo-induced electrons generated in TiO₂, photocatalytic oxidation of 3-methylpyridine was carried out in the absence of oxygen (under reduced pressure or under a nitrogen atmosphere). Under a nitrogen atmosphere and reduced pressure, the rate constants for oxidation of 3-methylpyridine did not change at all as shown in Figure 6. These results suggested that reduction of methylpyridine isomers proceeds dominantly instead of reduction of oxygen by photo-induced electrons in TiO₂ under the condition of photoirradiation. After photoirradiation, we observed some minor products containing 3-methylpiperidine generated as a result of reduction of 3-methylpyridine. Identification of other minor products is now under investigation.

3.5. Photocatalytic oxidation of 4-methylpyridine on TiO₂ powders having a mixture of anatase and rutile phases that were prepared by physically mixing rutile particles with small anatase particles

In order to further prove the synergism between rutile and anatase TiO₂ for oxidation of 4-methylpyridine, we physically mixed a rutile powder (CR-EL) with an anatase powder (ST-01). The pure rutile (CR-EL) powder and the anatase powder (ST-01) were added at various ratios, keeping the total amount at 50 mg, to a mixed solution of acetonitrile (4.0 g), and this mixture was sonicated for 30 min. After this mixing procedure, 4-methylpyridine was added to the suspension and the photocatalytic reaction was carried out.

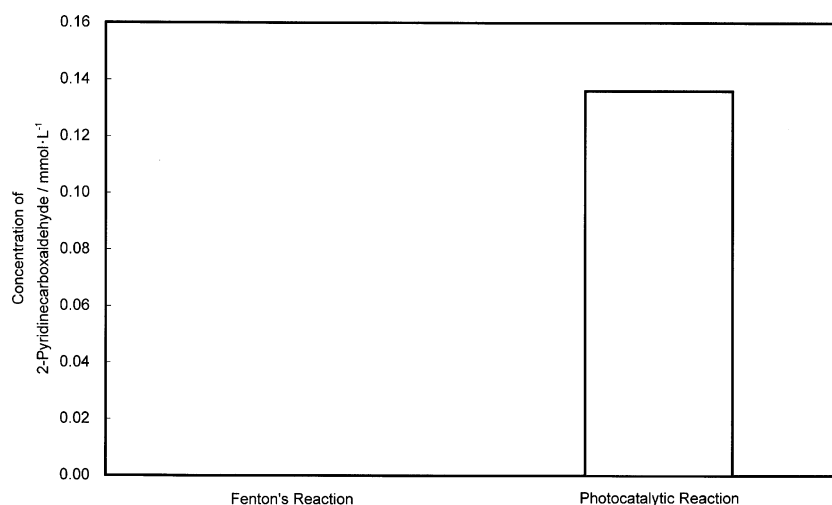


Fig. 5. Amounts of 3-pyridinecarboxaldehyde generated from 3-methylpyridine after photoirradiation for 1 h using Fenton's reagent. The reaction was carried out in a mixture of H₂O₂ (0.097 sc m, 5.0 ml) and FeCl₃·4H₂O (0.192 g) containing methylpyridine isomers (0.5 g). The reaction time was 5 min.

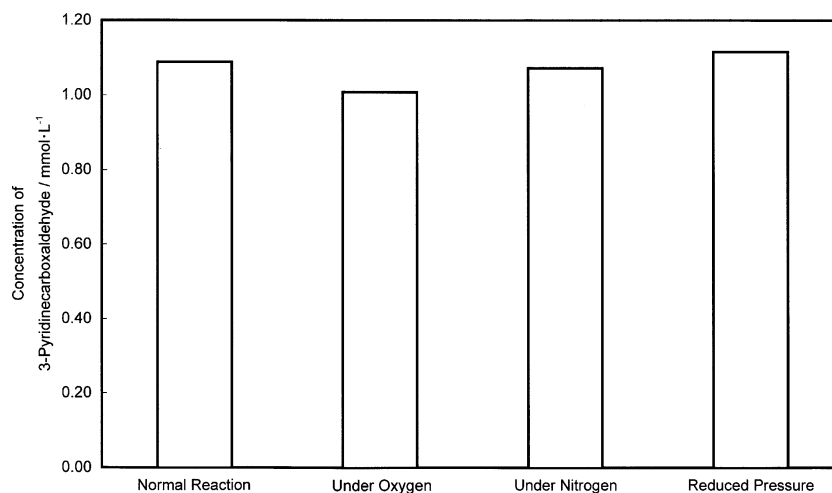


Fig. 6. Amounts of 3-pyridinecarboxaldehyde generated from 3-methylpyridine after photoirradiation for 1 h using several TiO₂ powders under an aerated condition, anaerated condition (reduced pressure), and nitrogen atmosphere. The experimental conditions are described in detail in Section 2.

Photocatalytic activity of the mixed powder is shown in Figure 7 as a function of the content of CR-EL (rutile) powder. An important point is that the mixed powders showed higher levels of activity than that of pure anatase or pure rutile powder. This result strongly suggests that there is a synergistic effect of anatase and rutile powders. Another important point is that the level of photocatalytic activity was increased by adding a small amount of the anatase ST-01 powder to the rutile CR-EL powder, whereas the increase in the level of activity was a fairly small when a small amount of the rutile powder was added to the anatase powder, i.e., the slope on the left hand side of the peak is smaller than that on the right hand side. These results suggest that the presence of a small amount of anatase phase is important for attaining a high level of photocatalytic activity.

Figure 8 shows SEM pictures of the anatase ST-01 (a) and rutile CR-EL (b) powders and the mixed (c) powder. The SEM picture of the mixed powder with 75% rutile (c), which showed the highest level of photocatalytic activity, reveals that the small anatase

particles are effectively loaded on each rutile particle. It should be noted that the activity level of this powder is higher than that of the P-25 powder. The optimal content of anatase particles in the photocatalyst is thought to be dependent on the mixing conditions and, probably, on the particle sizes of the original powders.

A low level of photocatalytic activity of anatase fine particles has also been observed for oxidation of water [6]. Photoelectrochemistry of rutile and anatase TiO₂ electrodes showed that band bending in TiO₂ is necessary for photooxidation of water on them [6]. TiO₂ powders consisting of particles smaller than 10 nm are disadvantageous for the development of sufficient band bending, leading to a low level of activity for oxidation of water. Although the photooxidation of 4-methylpyridine on TiO₂ electrodes has not been studied, the low level of activity of fine anatase particles suggests that band bending is necessary for this reaction. On the other hand, for the photocatalytic reactions of alcohols, it is known that small anatase particles show high levels of activity. Photoelectrochemistry has shown that these

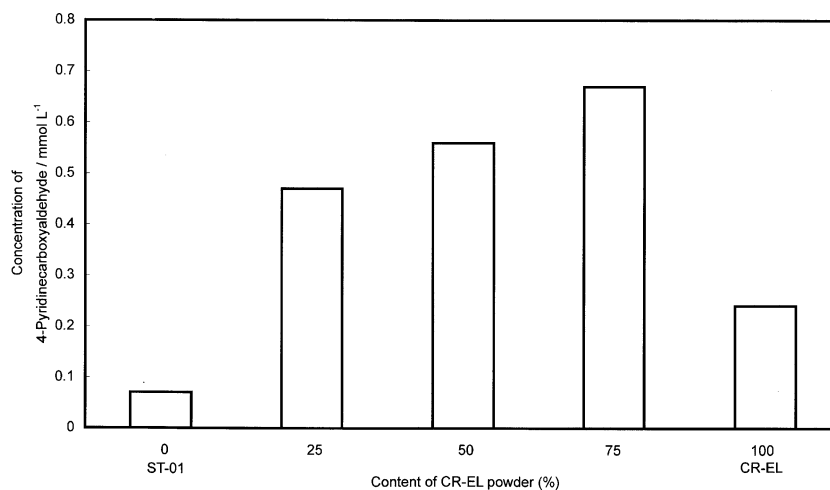


Fig. 7. Photocatalytic activities of TiO₂ powders prepared by mixing ST-01 powder with CR-EL powder at various ratios for the production of 4-pyridinecarboxaldehyde. Reaction conditions are the same as those for the experiment for which results are shown in Figure 1.

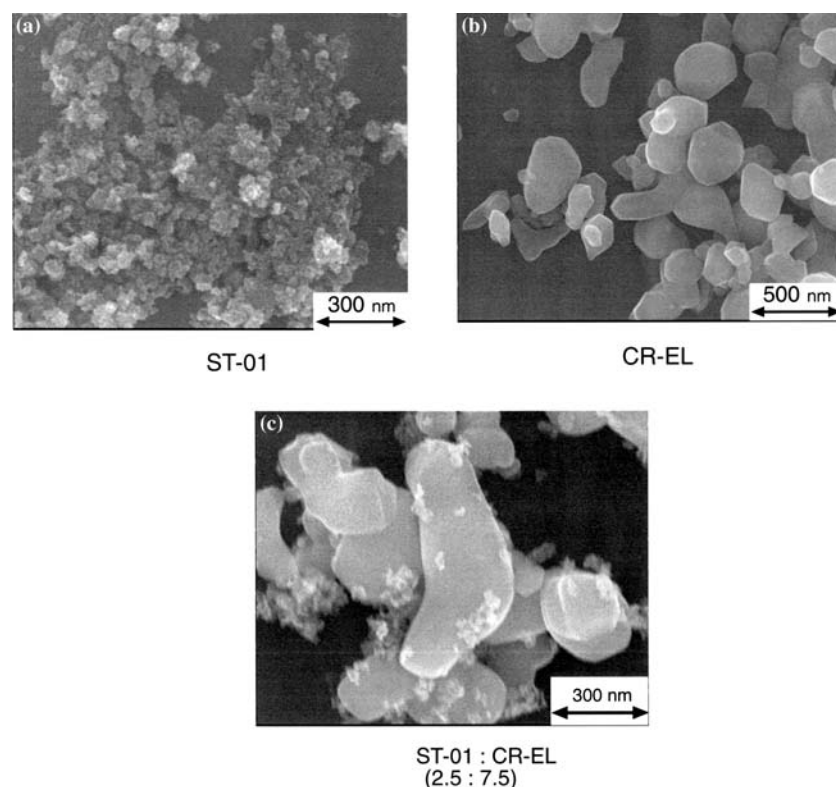


Fig. 8. SEM images of (a) ST-01 powder, (b) CR-EL powder, and their mixtures at ratios of (c) 25:75, respectively.

compounds are easily oxidized on TiO_2 electrodes without having large band bending [23].

The conduction band of anatase TiO_2 has been considered to be located at a higher energy position than that of rutile TiO_2 by about 0.2 eV [24]. This relationship of the energy levels is disadvantageous for electron transfer from rutile particles to anatase particles, which is assumed to be the reason for the synergistic effect of rutile and anatase particles, as described in Section 3.5. Under our experimental conditions, the possibility that electrons are transferred from rutile particles to anatase particles *via* thermal activation must be considered. This possibility is supported by the fact that electron transfer *via* energy barriers higher than 0.2 eV is a common practice in semiconductor and organic electronic devices [25, 26]. Although the mechanism remains to be clarified, all the results regarding the photocatalytic activities of the mixed TiO_2 particles demonstrate that the electrons are effectively transferred from rutile particles (or electrodes) to anatase particles. Similar improvement in photocatalytic activity with mixed TiO_2 powder has been reported [20, 27]. Consequently, charge separation between photogenerated electrons and holes is thought to be induced.

However, these improvements in photocatalytic activity for oxidation of 2- and 3-methylpyridine were not observed. Although the reason for the improvements in the reaction is not clear, their adsorbability on the surfaces of TiO_2 particles and the geometry of methyl-

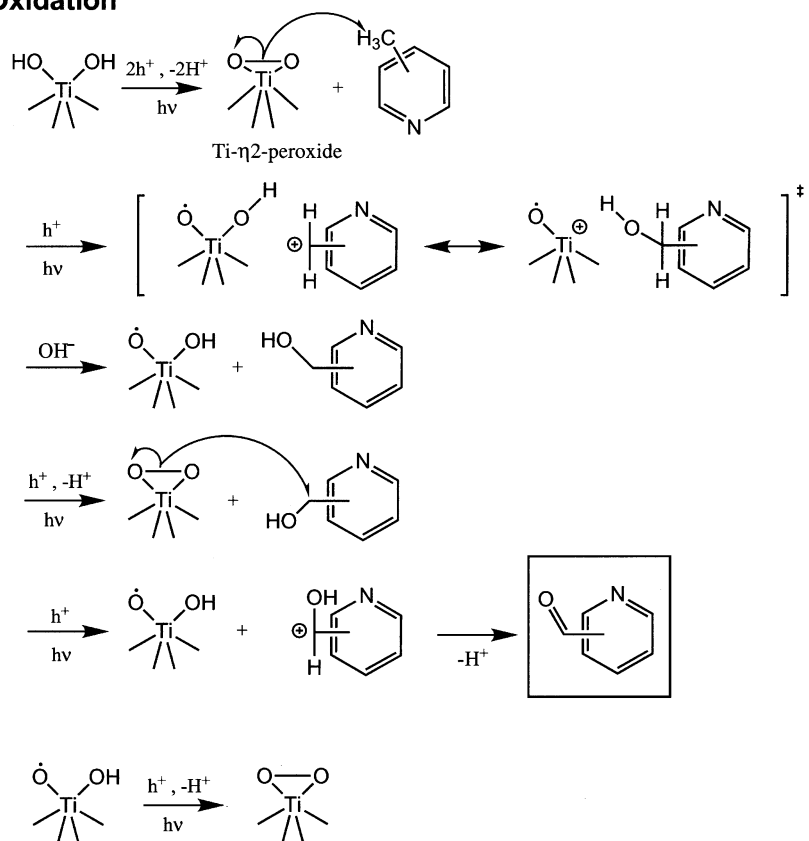
pyridine isomers adsorbed on the surface of TiO_2 particles are also thought to be important factors.

3.6. Proposed mechanism for TiO_2 -photocatalyzed oxidation of methylpyridine isomers

As discussed above, when methylpyridine isomers are oxidized by free OH radicals produced by Fenton's reagent, no product was obtained. This is because free OH radicals are not the main active species of the reaction as stated in the previous section. On the other hand, when methylpyridine isomers are oxidized on photoirradiated TiO_2 particles, pyridinecarboxaldehyde isomers are effectively generated as main products. This suggests that the active species involved in this reaction is not free OH radicals. We also found that the origin of oxygen introduced into pyridinecarboxaldehyde isomers as an aldehyde group comes from oxygen of water contained in acetonitrile solution. In addition to these results, it was found that the photocatalytic activity of TiO_2 increased when an appropriate amount of water was added to the solution. These results indicate that water plays an important role in the reaction.

On the basis of the results, we propose a mechanism, shown in Scheme 1, for the production of pyridinecarboxaldehyde isomers on the surfaces of TiO_2 particles under deep UV light. $\text{Ti}-\eta^2$ -peroxide dominantly generated on the surfaces of rutile TiO_2 particles is thought to be the active species. Under the condition of deep UV irradiation, one of the oxygen atoms in the peroxo

Oxidation



Scheme 1.

group is assumed to be transferred to the methylpyridine *via* a transition state, shown in Scheme 1. A similar transition state has been proposed for the catalytic epoxidation of olefins by TiO_2 as photocatalysts [28]. After detachment of the aldehyde, the Ti- η^2 -peroxide complex is regenerated as shown in Scheme 1. In the case of anatase particles, the Ti- η^2 -peroxide complex mainly generated on the surfaces of anatase TiO_2 particles under the condition of photoirradiation is thought to be inactive for oxidation of methylpyridine isomers, as it is inactive for the oxidation of olefins, naphthalene [21] and adamantane [29].

4. Conclusions

We found that photocatalytic oxidation of methylpyridine isomers effectively proceeded to generate pyridinecarboxaldehyde isomers as main products on TiO_2 under anaerated conditions. The rate of production of pyridinecarboxaldehyde depended on the TiO_2 powder used. We also found synergism between anatase and rutile particles for the photocatalytic oxidation of 4-methylpyridine, whereas no synergistic effect was observed for oxidation of 2- and 3-methylpyridine. By simply mixing these particles, higher levels of activity than those of the original powders were obtained. Furthermore, the level of activity is higher than those of many kinds of TiO_2 powders obtained from different sources. These results

are explained by assuming that rutile particles are advantageous for the oxidation of 4-methylpyridine. The combination of large rutile particles and small anatase particles is practically useful, because rutile particles are generally produced at high temperatures and are large, and anatase particles are produced at low temperatures and are small. We demonstrated that the synergism between rutile and anatase particles occurs for the oxidation of naphthalene only under aerated conditions. Small anatase particles loaded on large rutile particles are thought to be advantageous for the reduction of oxygen, probably because of the surface catalytic activity [20]. In this study, we showed that a similar effect exists in photocatalytic oxidation of 4-methylpyridine in the absence of oxygen.

The reaction is interesting from the viewpoint of organic syntheses, especially in connection with green chemistry, because a stable compound can be converted to aldehyde derivatives using water as the oxygen source by utilizing photon energy.

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