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Running title (photocatalytic oxidation of methylpyridine isomers on TiO₂)

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 TiO_2 particles for oxidation of 3-methylpyridine. A rutile fine particle showed the highest level of activity for the reaction. In addition to these results, 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 TiO_2 particles under the conditions used. These results suggest that the activities of TiO_2 photocatalysts for oxidation of methylpyridine isomers are dominated by the oxidation potential of alkylpyridine and band bending of TiO_2 particles.

Keywords: Titanium dioxide; Photocatalysts; Methylpyridine; Anatase; Rutile;

Pyridinecarboxaldehyde; Photooxidation; Synergy effect

1. Introduction

Titanium dioxide (TiO_2)-mediated heterogeneous photocatalysis has attracted great attention because of its potential applications to decomposition of pollutants in water and air.¹⁻⁵ TiO_2 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 TiO_2 photocatalysts.¹²⁻²⁰ In many applications, anatase TiO_2 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 phenols¹⁹ and olefins.¹⁶ In contrast to these compounds, oxidation of water efficiently proceeds on large rutile TiO_2 particles.^{4,5,9} It has been shown from photoelectrochemistry of TiO_2 electrodes that band bending is necessary for oxidation of water. Thus, it is thought that TiO_2 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 pyridinecarboxialdehyde isomers effectively proceeds on TiO_2 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 in this report.

2. Experimental

2.1. Materials and instruments

Various kinds of titanium dioxide (TiO₂) powders 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; ST-21: 100%, 56.1 m²/g; ST-41: 100%, 8.2 m²/g; CR-EL: 0%, 7.1 m²/g; AMT-100: 100 %, 290.0 m²/g; AMT-600: 100%, 59.0 m²/g; MT-150A: 0 %, 81.5 m²/g; TIO-3: 0%, 48.1 m²/g; TIO-5: 9%, 2.5 m²/g; P-25: 83.5%, 49.2 m²/g. 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 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 UV35 filter (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 K_2HPO_4 , 2.5 mM KH_2PO_4 and 0.1 M $NaClO_4$) 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 reagent²¹

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-mass spectroscopy. 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 H_2^{18}O (0.4 g). Methylpyridine isomers (2-methylpyridine, 3-methylpyridine or 4-methylpyridine) (0.5 g) and TiO_2 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 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 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 TiO_2 used are the same as those in the case of photocatalytic oxidations of methylpyridine isomers under an aerobic condition.

2.6. *Preparation of the TiO_2 powders containing rutile and anatase phases*

TiO_2 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 TiO₂ powder used as the photocatalyst, but 2-pyridinecarboxaldehyde was always the main product using any kind of TiO₂ powder. Among the TiO₂ powders we investigated, extremely large TiO₂ particles (CR-EL) having a pure rutile phase showed the highest level of photocatalytic activity for the production of 2-pyridinecarboxaldehyde as shown in Fig. 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 TiO₂ was much greater than that of anatase TiO₂ 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 TiO₂ powders as photocatalysts.

The main product of photooxidation of 3-methylpyridine was confirmed to be 3-pyridinecarboxaldehyde. Among the TiO₂ powders we investigated, a pure rutile powder (MT-150A) having a large surface area showed the highest level of

photocatalytic activity as shown in Fig. 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 adsorbability of 3-methylpyridine on the surface of TiO₂ and oxidation powder of TiO₂ is the most important factor for improving photocatalytic activity.

3.1.3. Photooxidation of 4-methylpyridine using TiO₂ powders as photocatalysts.

The rate of production of 4-pyridinecarboxaldehyde depended on the TiO₂ powder used, but 4-pyridinecarboxaldehyde was always the main product using any kind of TiO₂ powder as shown in Fig. 3. Among the TiO₂ powders we investigated, a powder (P-25) that contains both anatase and rutile particles²² 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 TiO₂ 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 TiO₂ powders for oxidation of methylpyridine isomers were greatly improved by addition of water to the acetonitrile solution as shown in Fig. 4. These results suggest that water is included in the reaction scheme for oxidation of methylpyridine isomers to generate pyridinecarboxyaldehyde 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 pyridinecarboxyaldehyde 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 Fig. 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.

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 Fig. 6. These results suggested that reduction of methylpyridine isomers is dominantly proceeds 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.

Photocatalytic activity of the mixed powder is shown in Fig. 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 compounds are easily oxidized on TiO₂ electrodes without having large band bending.²³

The conduction band of anatase TiO₂ has been considered to be located at a higher energy position than that of rutile TiO₂ 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 of the results regarding the photocatalytic activities of the mixed TiO₂ particles demonstrate that the electrons are effectively transferred from rutile particles

(or electrodes) to anatase particles. Similar improvement in photocatalytic activity with mixed TiO₂ powder has been reported.^{20,27} Consequently, a 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 TiO₂ particles and the geometry of methylpyridine isomers adsorbed on the surface of TiO₂ particles are also thought to be important factors.

3.6. Proposed mechanism for TiO₂-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 TiO₂ particles, pyridinecarboxaldehyde isomers are effectively

generated as main products. This result 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 TiO₂ 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 TiO₂ particles under deep UV light. Ti-η²-peroxide dominantly generated on the surfaces of rutile TiO₂ particles is thought to be the active species. Under the condition of deep UV irradiation, one of the oxygen atoms in the peroxy 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 TiO₂ as photocatalysts.²⁸ After detachment of the aldehyde, the Ti-η²-peroxide complex is regenerated as shown in Scheme 1. In the case of anatase particles, the Ti-η² 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, naphthalene²¹ and adamantane.²⁹

4. Conclusions

We found that photocatalytic oxidation of methylpyridine isomers effectively proceeded to generate pyridinedicarboxaldehyde 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, a higher levels of activity than those of the original powders was 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 is 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 sources by utilizing photon energy.

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Figure captions

Figure 1. Amounts of 2-pyridinecarboxaldehyde after photoirradiation for 1 h using several TiO₂ powders. The reaction was carried out in a CH₃CN (4.0 g) containing 2-methylpyridine (0.5 g) and TiO₂ 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 the Experimental section.

Figure 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 Fig. 1.

Figure 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 Fig. 1.

Figure 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 the Experimental section.

Figure 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 M, 5.0 mL) and FeCl₂•4H₂O (0.192 g) containing methylpyridine isomers (0.5 g). The reaction time was 5 min.

Figure 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 the Experimental section.

Figure 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 Fig. 1.

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

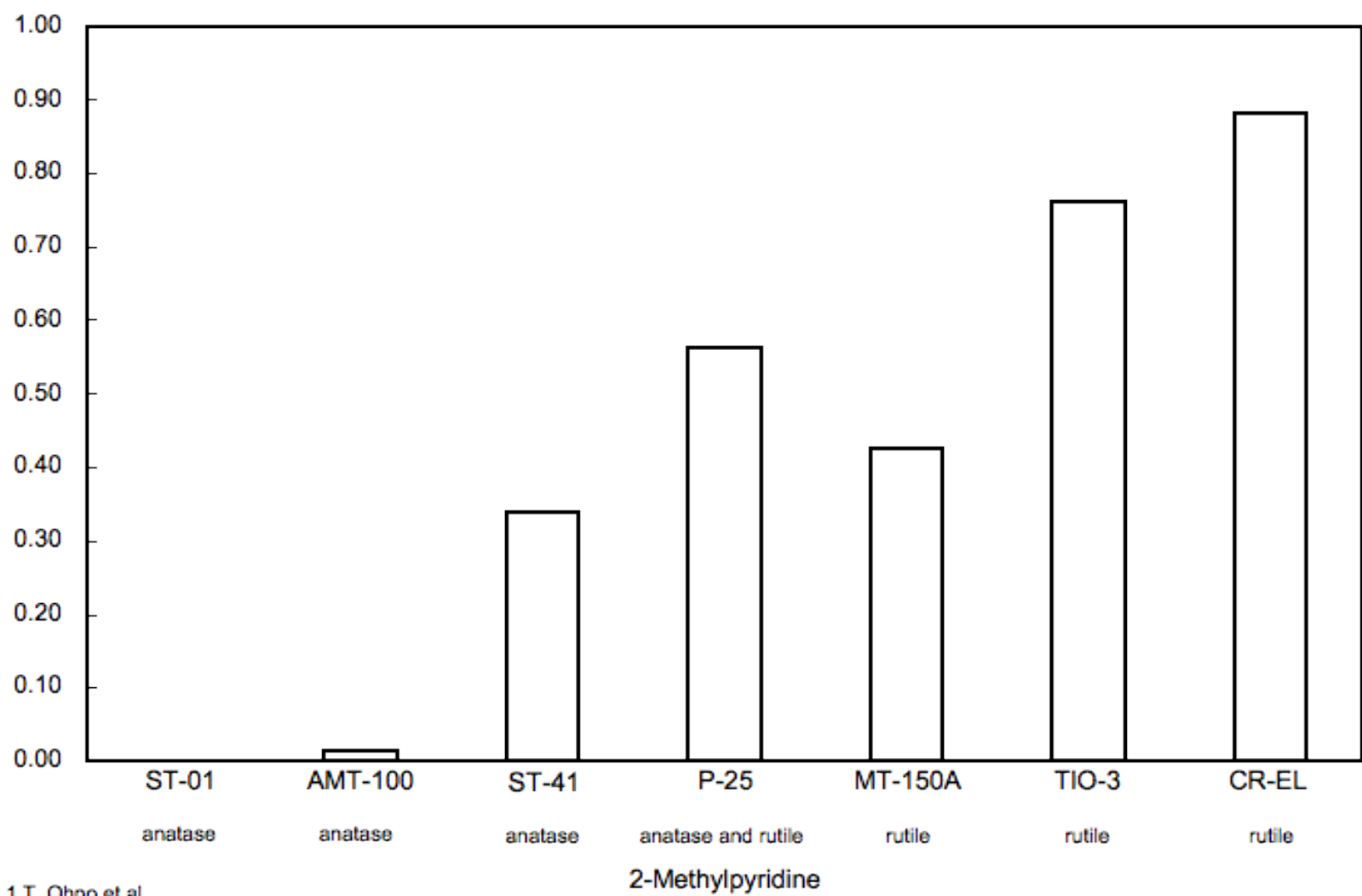


Fig. 1 T. Ohno et al.

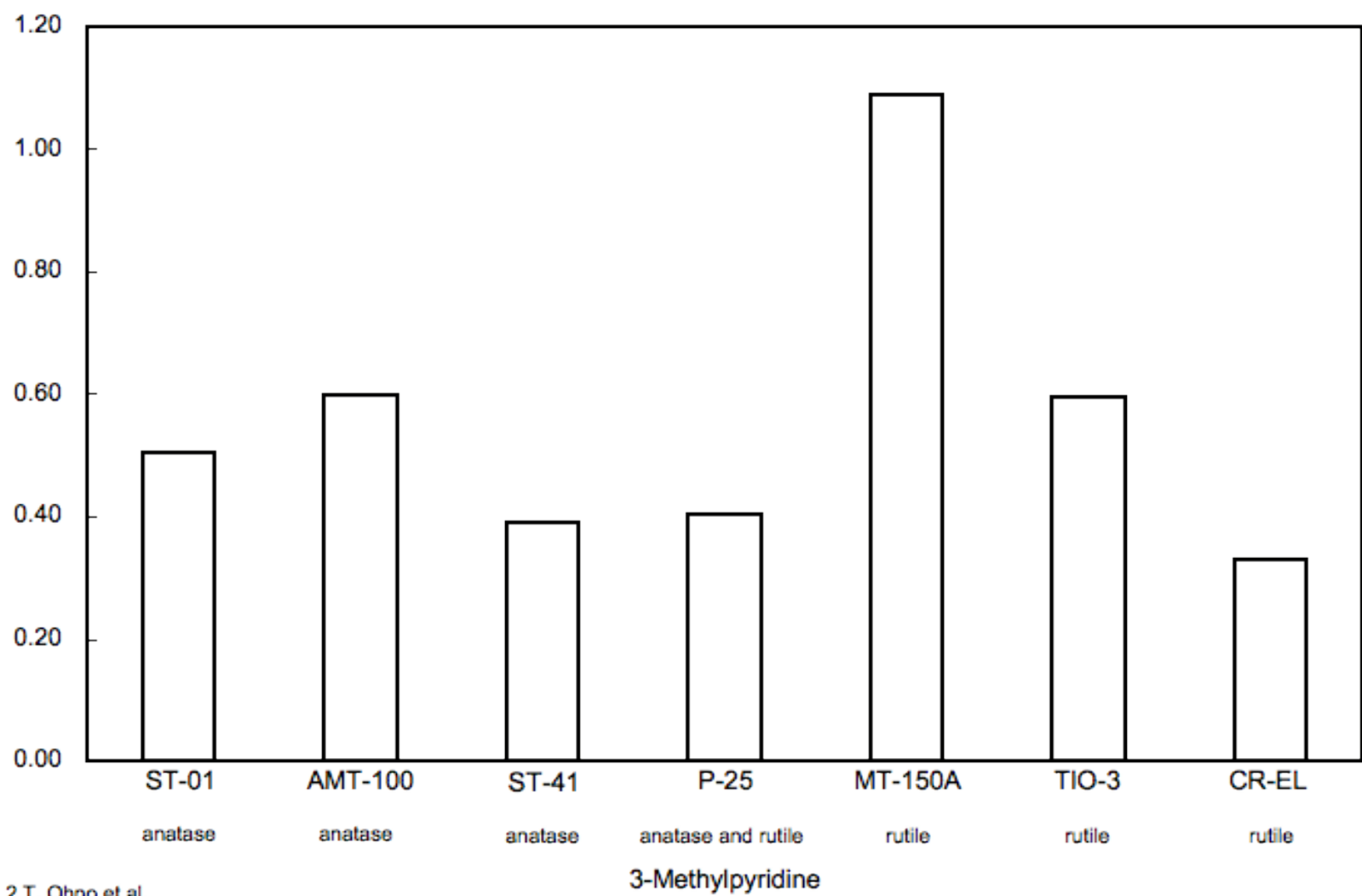


Fig. 2 T. Ohno et al.

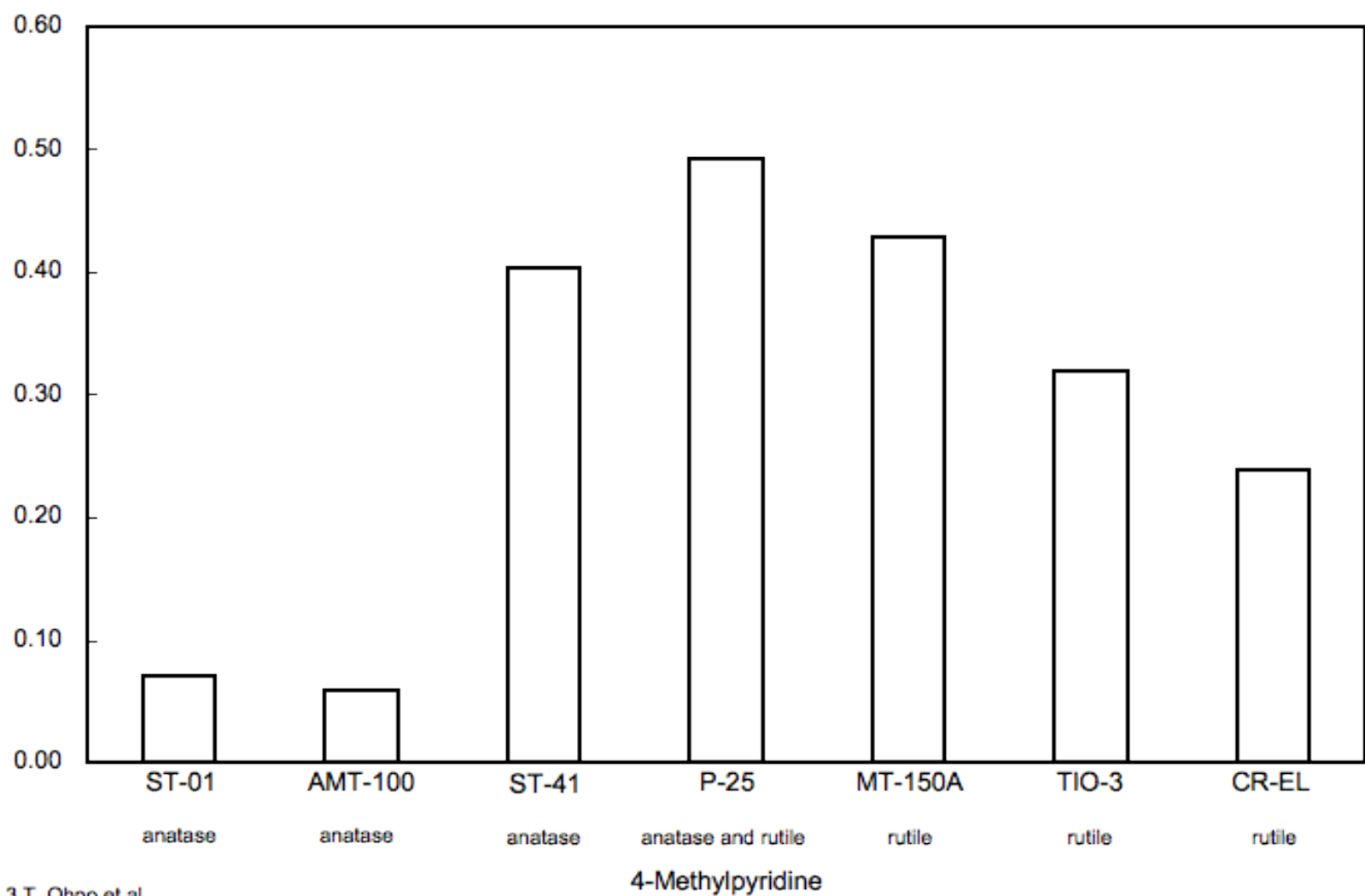


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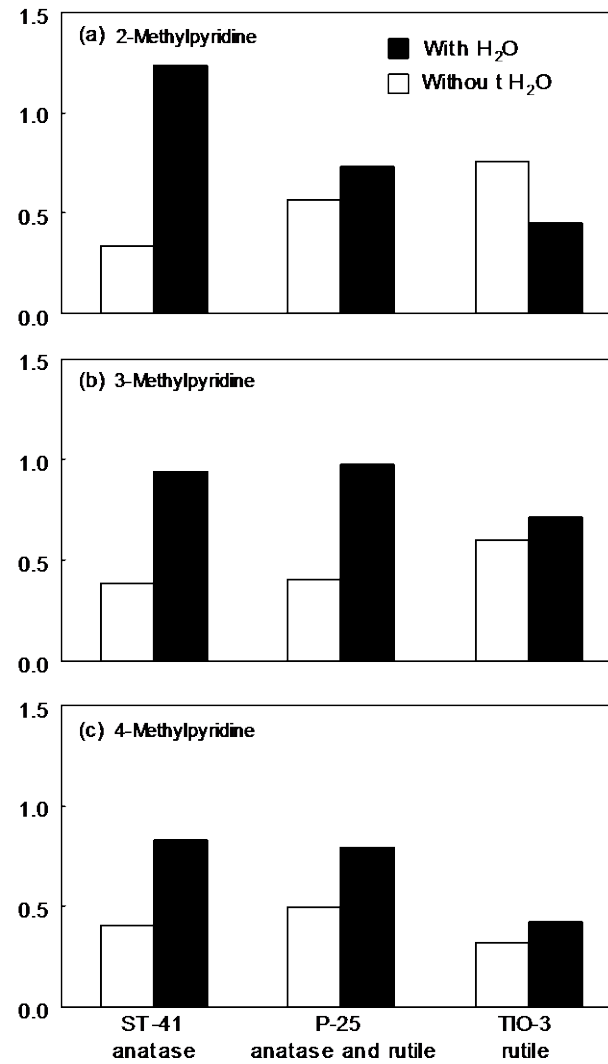


Fig. 4 T. Ohno et al.

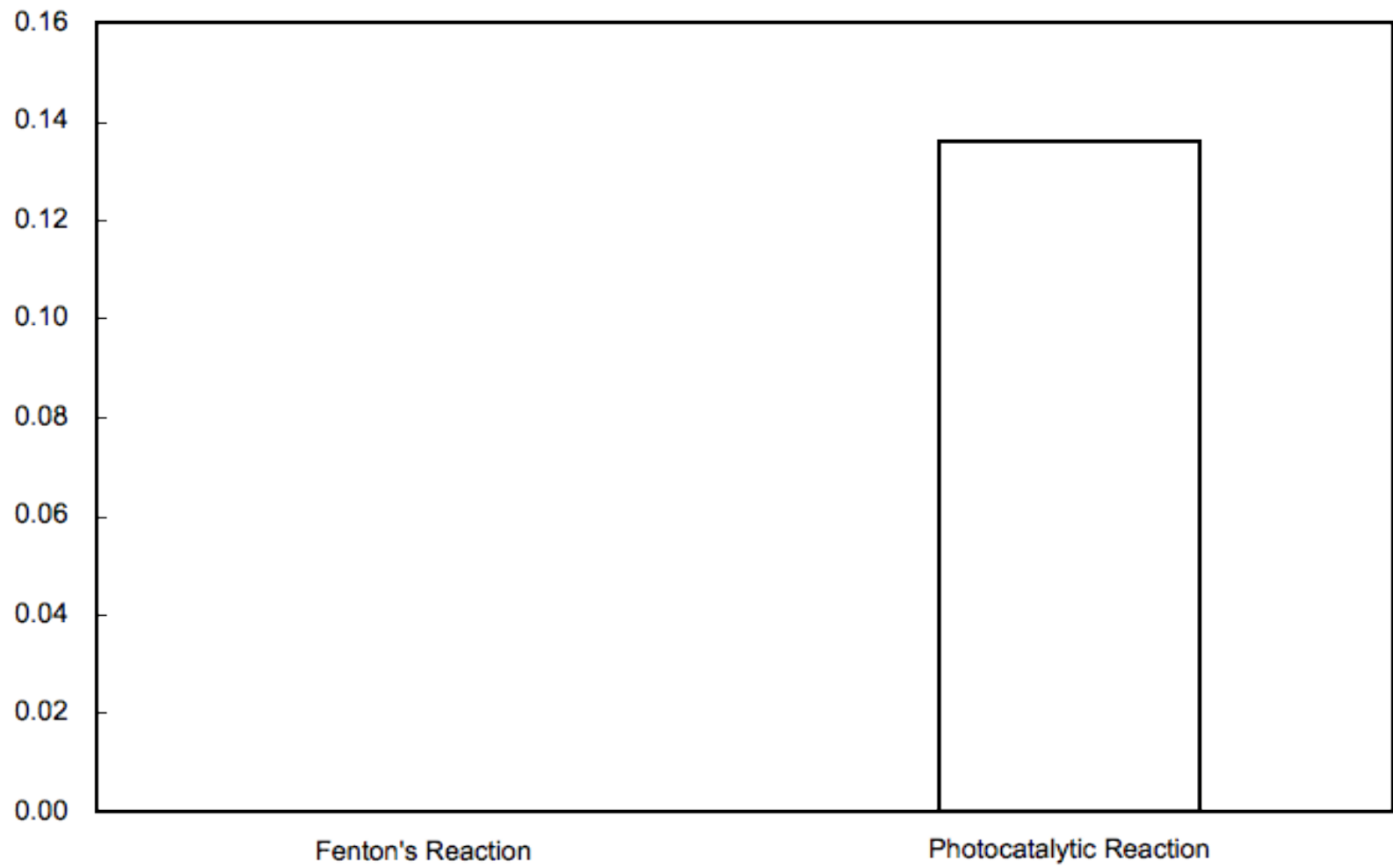


Fig. 5 T. Ohno et al.

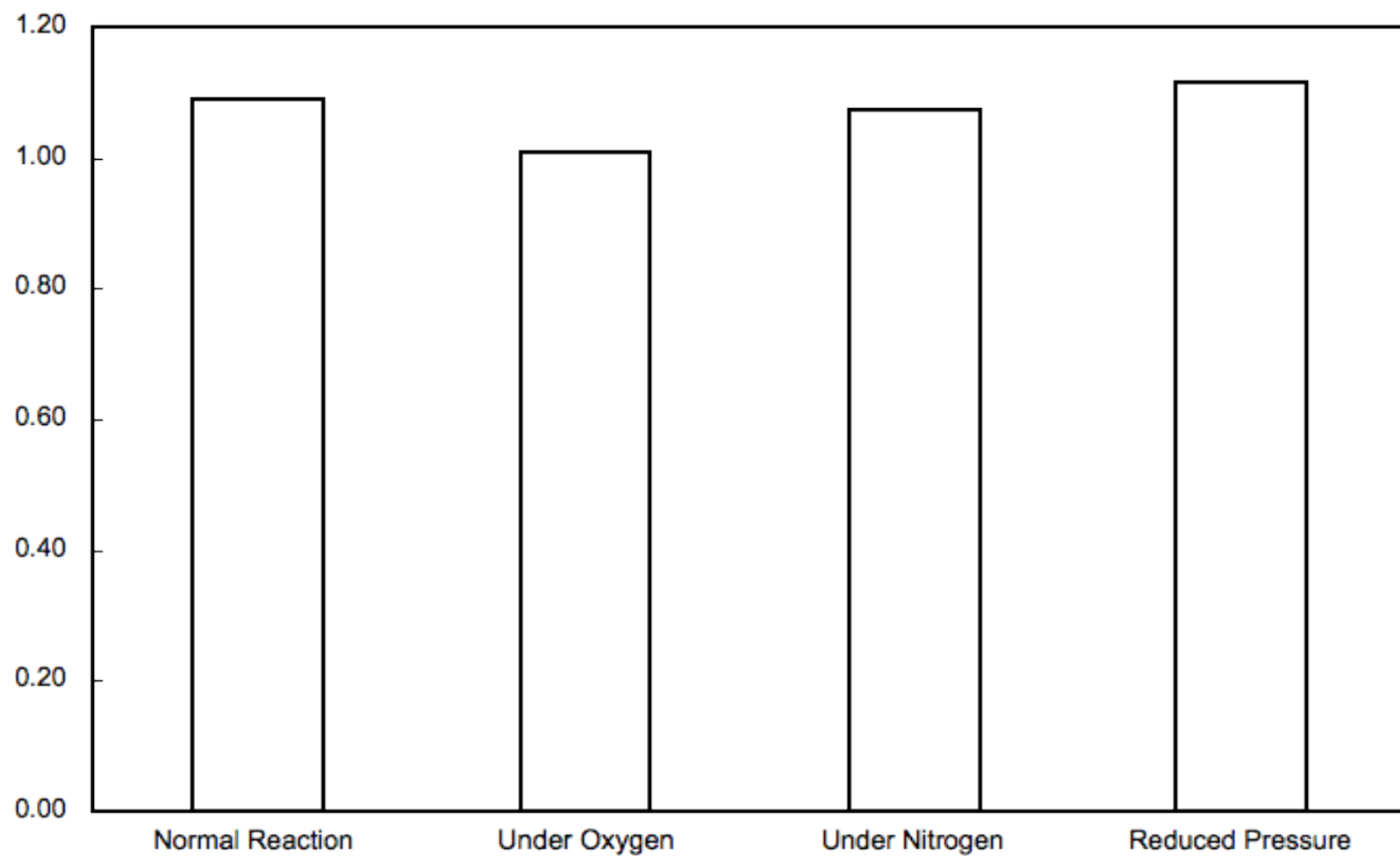


Fig. 6 T. Ohno et al.

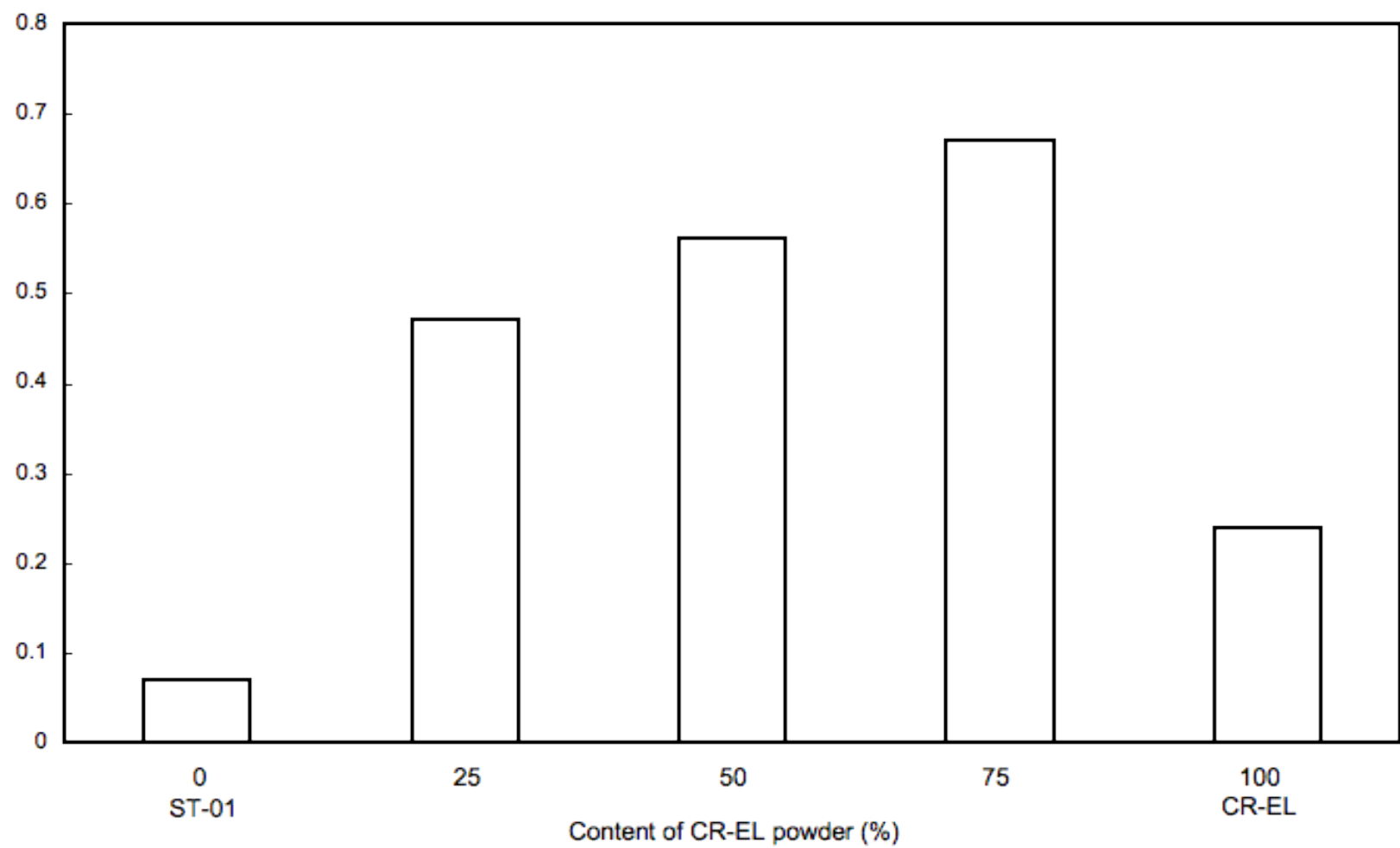
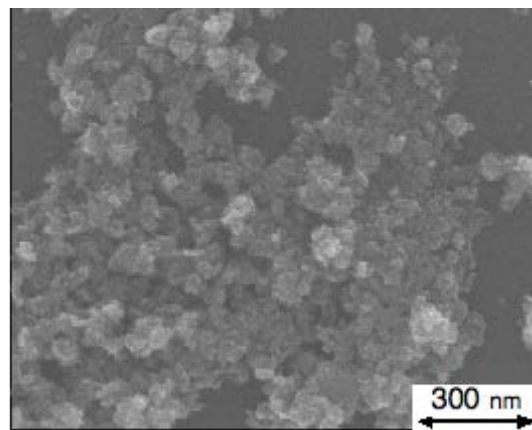
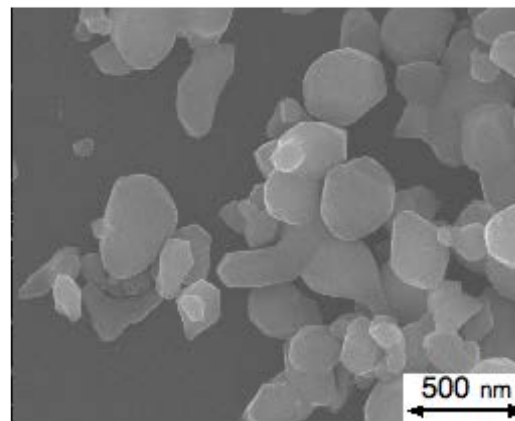


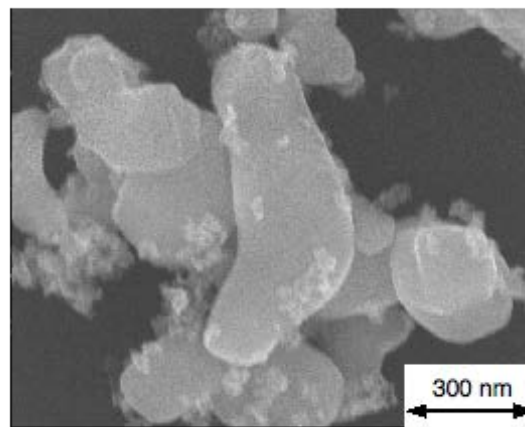
Fig. 7 T. Ohno et al.



(a) ST-01



(b) CR-EL



(c) ST-01 : CR-EL
(2.5 : 7.5)

Fig. 8 T. Ohno et al.