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Author(s)	Kominami, Hiroshi; Kumamoto, Hisayuki; Kera, Yoshiya et al.
Citation	Journal of Photochemistry and Photobiology A Chemistry, 160(1-2), 99-104 https://doi.org/10.1016/S1010-6030(03)00227-2
Issue Date	2003-08-07
Doc URL	https://hdl.handle.net/2115/17128
Type	journal article
File Information	JPPA160-1-2.pdf



Photocatalytic Decolorization and Mineralization of Malachite Green in An Aqueous Suspension of Titanium(IV) Oxide Nano-particles under Aerated Conditions: Correlation between Some Physical Properties and Their Photocatalytic Activity

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Abstract

Titanium(IV) oxide (TiO₂) nano-particles with various physical properties, which had been prepared by hydrothermal crystallization in organic media (HyCOM) and post-calcination, were used for photocatalytic decomposition of malachite green (MG) in an aqueous suspension under aerated conditions. The amount of MG adsorbed on TiO₂ ([MG]_{ad}) increased as the surface area of HyCOM TiO₂ increased. The apparent initial rate constant of **pseudo** zero-order kinetics, k_0 , for decolorization of MG in an early stage (~15 min) coincided well with [MG]_{ad}, indicating that adsorptivity is a decisive factor for the initial bleaching of MG. However, in a 1 h irradiation experiment, a HyCOM sample with a smaller [MG]_{ad} but improved crystallinity exhibited higher decolorization activity than did HyCOM TiO₂ with the largest [MG]_{ad}, suggesting that this reaction process includes deactivation of the photocatalyst due to deposition of intermediate(s) that had been formed by degradation of MG. Longer irradiation was required for mineralization of MG. Total organic carbon (TOC) in the suspension of HyCOM TiO₂ with improved crystallinity continuously decreased whereas TOC in Degussa P-25 TiO₂ did not decrease any more after 5

h of irradiation, although one third of the initial TOC still remained in the suspension.

Keywords: Titanium(IV) oxide; Photocatalyst; Decolorization; Mineralization

1. Introduction

Photocatalytic decomposition (or mineralization) of organic compounds, such as environmentally toxic compounds, and photocatalytic decolorization of dyes in industrial waste water under aerated conditions have been studied extensively in recent years [1-6]. Most studies have focused on decomposition mechanisms, intermediate(s), effects of experimental conditions and possibility of environmental application. Commercially available Degussa P-25 TiO₂ has been used in most such studies since it exhibits a relatively high level of photocatalytic activity in various reaction systems. In some studies, photocatalysts prepared by hydrolysis of alkoxides and post-calcination were used. However, precise control of the physical properties of TiO₂ by calcination is generally difficult because growth of anatase crystallite and transformation into rutile crystallite occur upon calcination at >773 K. There have thus been few reports on the correlation between physical properties and photocatalytic activity. To achieve effective decomposition of organic compounds, design and development of photocatalysts with high levels of activities are needed. Some investigators have tried to enhance the efficiency of photocatalytic reactions using TiO₂-based photocatalysts [7,8]. Bard *et al.* [7] prepared TiO₂-SiO₂ composite photocatalysts and used them for decomposition of Rhodamine-6G (R6G). SiO₂ possesses greater ability to adsorb R6G, the TiO₂-SiO₂ composite photocatalysts exhibited a higher level of decomposition activity than that of P-25 TiO₂. However, the effects of the properties of TiO₂ itself are unclear.

We have reported that nano-crystalline TiO₂ can be synthesized by the HyCOM (Hydrothermal Crystallization in Organic Media) method and that a wide range of physical

properties, e.g., crystallinity and surface area, can be controlled by post-calcination [9,10]. We have examined the correlations between physical properties and photocatalytic activities of HyCOM TiO₂ in several reaction systems and have found that the crystallinity of TiO₂ influenced the activity in different ways depending on the type of photocatalytic reaction [11-15]. In oxygen (O₂) evolution from an aqueous suspension of TiO₂ powders, TiO₂ with a higher degree of crystallinity, i.e., less defects, exhibited a higher level of activity, suggesting that recombination of a photogenerated electron-hole pair (e⁻-h⁺) is a decisive factor in this system [13-15]. In mineralization of acetic acid in an aerated TiO₂ suspension, TiO₂ powders with larger surface areas, i.e., higher adsorptivity, showed a higher rate of CO₂ formation, indicating that adsorption of acetic acid is important in this system [12]. Once one hole reacts with acetic acid adsorbed on TiO₂ surface, successive oxidation by O₂ dissolved in the liquid phase proceeds thermally [16], indicating that decomposition of acetic acid is relatively simple. On the other hand, decomposition of organic compounds consisting of large molecules such as dye seems to be difficult and complicated, and the property required for effective degradation of acetic acid, i.e., a high level of adsorptivity, might have no effect for decomposition of organic compounds consisting of large molecules. In this study, we prepared HyCOM TiO₂ powders with various physical properties and used them for photocatalytic decomposition of malachite green (MG), which was chosen as a model dye. Correlations between some physical properties and the photocatalytic activity of HyCOM TiO₂ were investigated.

2. Experiment

2.1. Synthesis and characterization of HyCOM TiO₂ powders

HyCOM TiO₂ powders were synthesized according to the procedure previously reported [10-15]. Titanium(IV) butoxide (Kanto Chemical, Tokyo, Japan) was dissolved in toluene (70 cm³) in a test tube, and the test tube was then set in a 200 cm³ autoclave. The

gap between the test tube and the autoclave wall (5 cm^3) was filled with water. The autoclave was thoroughly purged with nitrogen, heated to 573 K at a rate of 2.5 K min^{-1} , and kept at that temperature for 2 h. After the treatment in the autoclave, the resulting powder was washed repeatedly with acetone and dried in air at ambient temperature. As-prepared HyCOM was calcined in a furnace at various temperatures under a flow of air ($30 \text{ cm}^3 \text{ min}^{-1}$); each sample was heated to the desired temperature (T_c) at a rate of 10 K min^{-1} , kept at that temperature for 1 h, and then cooled to room temperature. Each thus-calcined sample is designated as HyCOM(T_c), e.g., a sample calcined at 973 K is designated as HyCOM(973).

Powder X-ray diffraction (XRD) (RINT 2500, Rigaku) was measured using $\text{CuK}\alpha$ radiation with a carbon monochromator. Crystallite size was calculated from the half-height width of the 101 diffraction peak of anatase using the Scherrer equation. The value of the shape factor, K , was taken to be 0.9. The specific surface area (S_{BET}) was calculated using the BET single-point method on the basis of nitrogen (N_2) uptake measured at 78 K at the relative pressure of 0.3. Before the N_2 adsorption, each sample was dried at 403 K for 30 min in a 30% N_2 -helium flow. Thermogravimetry (TG) and differential thermal analysis (DTA) (TG-8120, Rigaku) were conducted at a rate of 10 K min^{-1} in air flow.

2.2. Adsorption and photocatalytic decomposition of MG in an aqueous suspension of TiO_2 under aerated conditions

TiO_2 (50 mg) was suspended in 5 cm^3 of MG ($0.54 \mu\text{mol}$) solution ($108 \mu\text{mol dm}^{-3}$) and photoirradiated at a wavelength of $> 300 \text{ nm}$ by a black light lamp (10 W) under air at 298 K with magnetic stirring. The amount of CO_2 in the gas phase was measured by a Shimadzu GC-8A gas chromatograph equipped with a Porapak QS column. The TiO_2 -suspended solution was centrifuged, and the MG concentration in the supernatant was measured from its absorbance at 611 nm. MG adsorption, $[\text{MG}]_{\text{ad}}$, in the dark was calculated under conditions similar to those used for the photocatalytic reaction from the difference between MG concentrations before and after the addition of TiO_2 into MG solutions of various

concentrations. Concentrations of total organic carbon (TOC) and total inorganic carbon (TIC) in the liquid phase were determined with a TOA DKK LASA-20 spectrophotometer using kits specified for measurement of each component.

3. Results and Discussion

3.1. Physical properties of HyCOM TiO₂ samples and adsorption of MG

Figure 1 shows XRD patterns of HyCOM TiO₂ samples obtained by calcination of as-synthesized HyCOM TiO₂ at various temperatures. HyCOM(823) and HyCOM(973) consisted of anatase crystallite [17], and only a small amount of the rutile phase [18] was observed in HyCOM(1073). The rutile phase was predominant after calcination at 1173 K. However, anatase crystallite was still observed in HyCOM(1273). Crystallite size and specific surface area of these samples are summarized in **Table 1**. Crystallite size of these samples gradually increased, whereas S_{BET} decreased with elevation in Tc. Therefore, TiO₂ samples with various physical properties were obtained by calcination of as-synthesized HyCOM TiO₂. Thus-obtained TiO₂ samples were used for adsorption experiments and photocatalytic reactions.

Figure 2 shows the effects of Tc on $[\text{MG}]_{\text{ad}}$ of HyCOM TiO₂ samples. HyCOM(823), which had the largest S_{BET} , showed the largest $[\text{MG}]_{\text{ad}}$ ($0.60 \mu\text{mol g}^{-1}$). Further increase in Tc resulted in monotonic decrease in $[\text{MG}]_{\text{ad}}$. However, a linear correlation was not observed between S_{BET} and $[\text{MG}]_{\text{ad}}$ of HyCOM TiO₂ samples, in contrast to results previously obtained for adsorption of acetic acid [15] and silver ion (Ag^+) [13,15] on HyCOM TiO₂ samples, indicating that the adsorption behavior of MG is complex compared with the adsorption behavior of simple molecules and small ions. **Figure 2** also shows the effect of Tc on the amount of MG adsorbed per unit surface area of HyCOM TiO₂ ($[\text{MGs}]_{\text{ad}}$). As expected from the non-linearity between S_{BET} and $[\text{MG}]_{\text{ad}}$, $[\text{MGs}]_{\text{ad}}$ was not constant, and $[\text{MGs}]_{\text{ad}}$ increased with elevation in Tc, i.e., decrease in S_{BET} . Since an MG molecule is

much larger than an acetic acid molecule or Ag^+ and has various functional groups, its adsorption may be also affected by other factors such as pore size, density of surface hydroxyl groups, and hydrophobicity of the TiO_2 surface. The cross-sectional area of an MG molecule (S_{MG}) was roughly estimated to be $1.6 \text{ nm}^2 \text{ molecule}^{-1}$ based on the assumption that an MG molecule is circular and has a diameter of 1.42 nm. The value, $0.39 \mu\text{mol m}^{-2}$, calculated from the equation $1/(A \cdot S_{\text{MG}})$, where A is Avogadro's constant, means the maximal $[\text{MGs}]_{\text{ad}}$ when MG molecules horizontally adsorb to the surface of TiO_2 . This value is larger than $[\text{MGs}]_{\text{ad}}$ experimentally obtained for all HyCOM TiO_2 samples, indicating that MG adsorbed horizontally to the surface of TiO_2 . $[\text{MG}]_{\text{ad}}$ and $[\text{MGs}]_{\text{ad}}$ for Degussa P-25 TiO_2 were determined to be $0.193 \mu\text{mol g}^{-1}$ and $0.0039 \mu\text{mol m}^{-2}$, respectively, indicating that interaction between the P-25 surface and MG molecules is much weaker than that for HyCOM TiO_2 samples. The amount of MG adsorbed on 50 mg of HyCOM(823) was calculated to be $0.030 \mu\text{mol}$, which is 5.6% of the amount of MG in the starting solution ($0.54 \mu\text{mol}$). Therefore, the observed decrease in MG concentration under UV irradiation in the presence of TiO_2 , which will be discussed in the next section, means that MG was decomposed photocatalytically.

3.2. Photocatalytic decolorization of MG in an aqueous suspension of TiO_2 in an early stage.

Time-dependency of MG concentration in an aqueous suspension of HyCOM(1073) in the initial 15 min of irradiation is shown in **Figure 3**. The concentration of MG linearly decreased just after photoirradiation, indicating pseudo zero-order kinetics for decolorization of MG in an early stage under the present conditions. The apparent rate constant, k_0 , was calculated from the slope of the plot. Similarly, the values of k_0 for HyCOM(823) and P-25 were determined and are shown in **Table 2**. HyCOM(823) exhibited a k_0 value 3.5-times larger than that for P-25, indicating that HyCOM(823) possessed a much higher level of photocatalytic activity for MG decolorization. Calcination at 1073 K decreased k_0 , but it

was still larger than that for P-25. A linear correlation was observed between k_0 and $[MG]_{ad}$, as shown in **Figure 4**, indicating that adsorption ability of TiO_2 toward MG determines the rate of MG decolorization in an early stage. Adsorption densities of MG on these three TiO_2 samples were different, as mentioned in the previous section, and the probability of electron and positive hole recombination, which is also an important factor determining photocatalytic activity, might be different. However, the initial degradation of MG was not affected by these factors. A similar adsorption effect on photocatalytic activity has been observed in mineralization of acetic acid in an aqueous suspension of HyCOM TiO_2 [15]. The molecular weight of MG is 927, and the process of decomposition (mineralization) of MG, which is described later, is complicated. However, it is clear that decolorization of MG, i.e., degradation of chromophore in MG molecules, proceeded relatively easily and that the rate of decolorization of MG depended on only $[MG]_{ad}$.

3.3. MG decomposition with prolonged irradiation

The amount of MG decolorized after 1 h of irradiation ($MG_{decolor}$), calculated from the decrease in concentration of MG in an aqueous suspension of HyCOM TiO_2 , is shown in **Figure 5**. $MG_{decolor}$ increased with increase in Tc and reached a maximum by calcination at 1073 K. Further increase in Tc resulted in a decrease in $MG_{decolor}$. However, all of the HyCOM samples except for HyCOM(1273) decolorized 60-80% of MG within only 1 h. Comparison with $MG_{decolor}$ for P-25 TiO_2 (0.266 μ mol) clearly shows that HyCOM TiO_2 samples possessed higher decolorization activity toward MG. The results obtained using HyCOM TiO_2 samples also indicate that the Tc-dependency of $MG_{decolor}$ was different from that of the initial decolorization, i.e., k_0 . HyCOM(823) showed a larger k_0 but a smaller $MG_{decolor}$ than those of HyCOM(1073), indicating that HyCOM(823) is deactivated in an early stage. Deposit of an intermediate(s) that was formed by decolorization of MG is probably attributed to the deactivation. Another property, e.g., high degree of crystallinity, may be

required in TiO₂ for effective decomposition of the intermediate(s).

Changes in MG concentration and TOC in aqueous suspensions of HyCOM(1073) and P-25 and changes in the amounts of CO₂ in the gas phase with elapse of irradiation time are shown in **Figure 6**. Decolorization of MG in the suspension of HyCOM(1073) occurred immediately after irradiation, while decolorization in the suspension of P-25 proceeded gradually. Since degradation of chromophore of MG depended on [MG]_{ad}, as stated in the previous section, the higher level of decolorization activity for HyCOM(1073) is reasonable ([MG]_{ad}: 0.457 μmol g⁻¹ for HyCOM(1073) vs. 0.193 μmol g⁻¹ for P-25). For HyCOM(1073), the MG concentration decreased to *ca.* 20% of the initial value after 1 h of irradiation, and most of the MG was decolorized after 2 h of irradiation, while TOC in the liquid phase decreased to *ca.* 60% of the initial value, indicating that a large amount of the intermediate(s), formed by decomposition of MG molecules, remained in the liquid phase. The gradual decrease in TOC suggests that decomposition of the intermediate(s) is difficult compared with bleaching of MG. The amount of TOC in the suspension of P-25 did not decrease any more after 5 h of irradiation. The amount of carbon dioxide, which is a final decomposition product, gradually increased with prolongation of irradiation time in both TiO₂ samples. The CO₂ yield for HyCOM(1073) was smaller than that for P-25, although the amount of TOC in the former was smaller than that in the latter. Amounts of TOC and TIC in the liquid phase and CO₂ in the gas phase are shown in **Table 3**. The amounts of total carbon (TC) for HyCOM(1073) and P-25 were 282 and 351 μg, respectively. TC for P-25 was consistent with TC corresponding to starting MG (338 μg) within an experimental error, while TC for HyCOM(1073) was smaller. The result obtained for HyCOM(1073) indicates that a large amount of the intermediate(s) is adsorbed on HyCOM(1073). In fact, the color of HyCOM(1073) after 10 h of reaction was purple, and 0.5% of weight loss was observed in the TG curve of the recovered sample. These results also indicate that P-25 was **partially** deactivated due to adsorption of only a small amount of the intermediate(s), while

HyCOM(1073) was still active for complete decomposition of the intermediate(s) into CO₂.

Conclusions

HyCOM TiO₂ samples with various physical properties were prepared and used for photocatalytic decomposition of MG in an aqueous solution under aerated conditions. HyCOM TiO₂ samples exhibited higher level of activity than did a commercial P-25 TiO₂ photocatalyst in this reaction as well as in other reaction systems. The apparent rate constant for initial decolorization of MG coincided well with [MG]_{ad}, indicating that [MG]_{ad}, i.e., adsorptivity, is a decisive factor for bleaching of MG. However, HyCOM TiO₂ with a smaller surface area and [MG]_{ad} but with improved crystallinity exhibited a higher level of decolorization activity than did the HyCOM sample with the largest [MG]_{ad} in prolonged irradiation, suggesting that this reaction included deactivation of the photocatalyst due to deposition of an intermediate(s) on the TiO₂ surface and that a high degree of crystallinity is required for continuous decomposition of MG into CO₂. The results obtained in this study show that deactivation of a photocatalyst should be studied for its industrial application. We are now investigating deactivation of TiO₂ photocatalysts in detail and methods for regenerating deactivated photocatalysts.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government. The author (H. K.) acknowledges the financial support from Kinki University.

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Kominami et al., Photocatalytic Decomposition of Malachite Green
Submitted to J. Photochem. Photobio. A: Chem.
07.1.18, 10:21 AM

837-841.

[17] JCPDS Card No. 21-1272

[18] JCPDS Card No. 21-1276

Figure captions

Figure 1. XRD patterns of HyCOM TiO₂ samples obtained by calcination of as-synthesized HyCOM TiO₂ at 823 (a), 973 (b), 1073 (c), 1173 (d) and 1273 K (e).

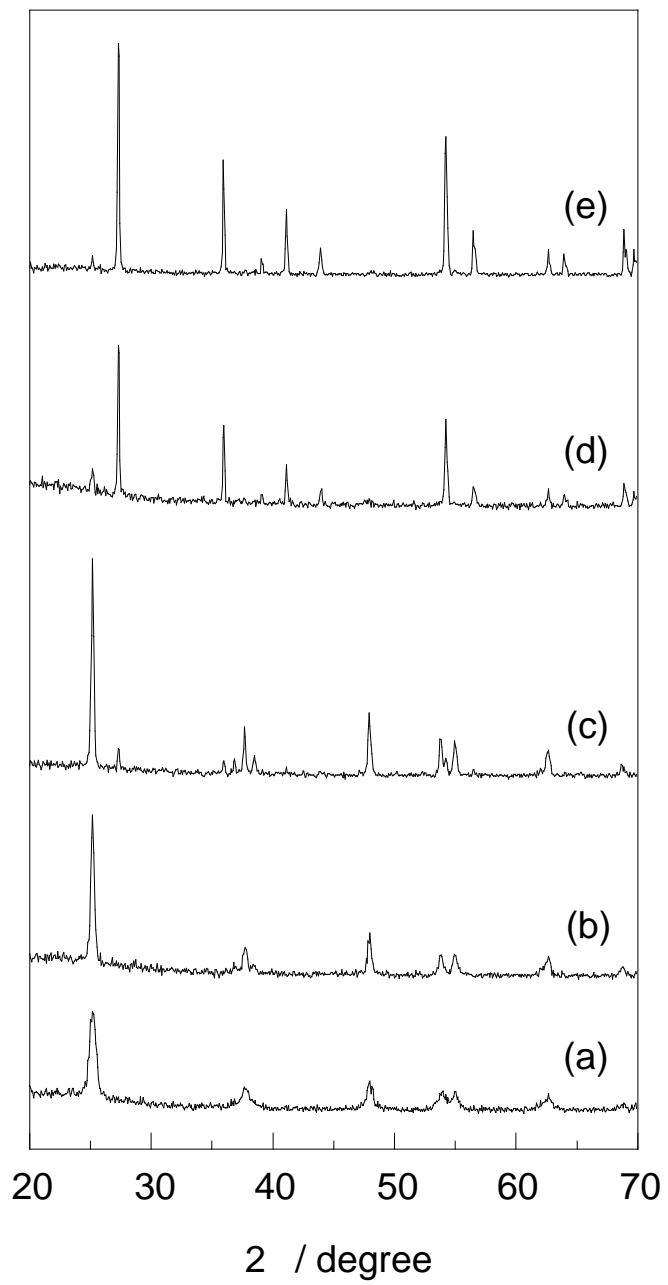
Figure 2. Tc-dependency of the amount of MG adsorbed per unit weight ($[MG]_{ad}$) and per unit surface area ($[MGs]_{ad}$) of HyCOM TiO₂

Figure 3. Time-dependency of MG concentration in an aqueous suspension of HyCOM(1073) in the initial 15 min of irradiation.

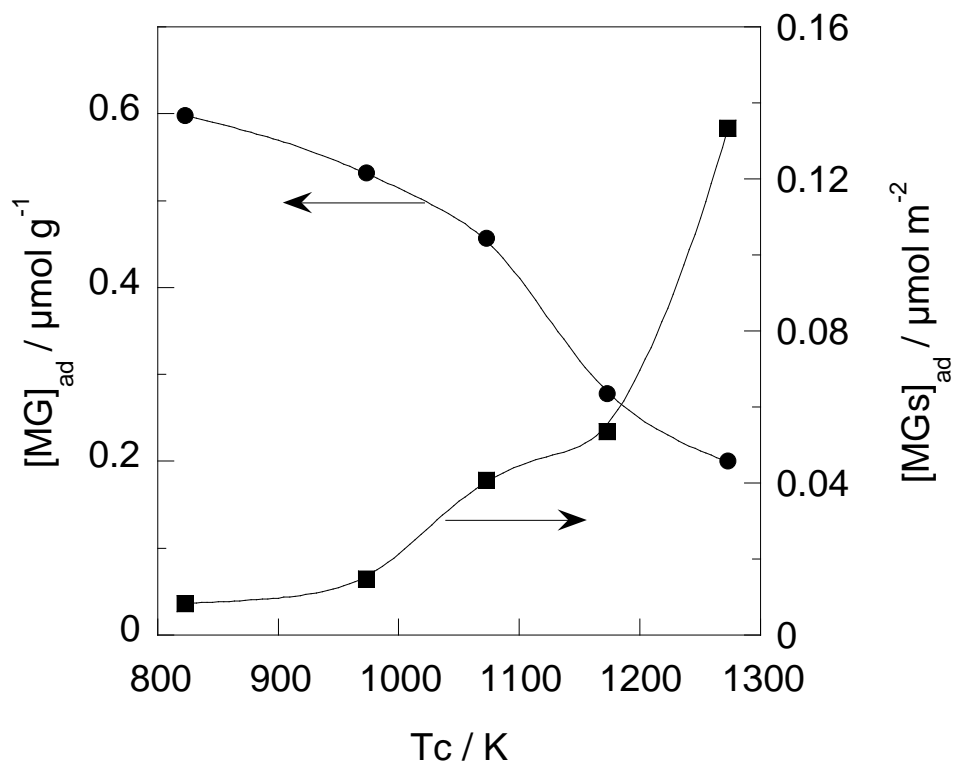
Figure 4. Correlation between k_0 and $[MG]_{ad}$.

Figure 5. Tc-dependency of MG decolorized after 1 h of irradiation (MG_{decold}),

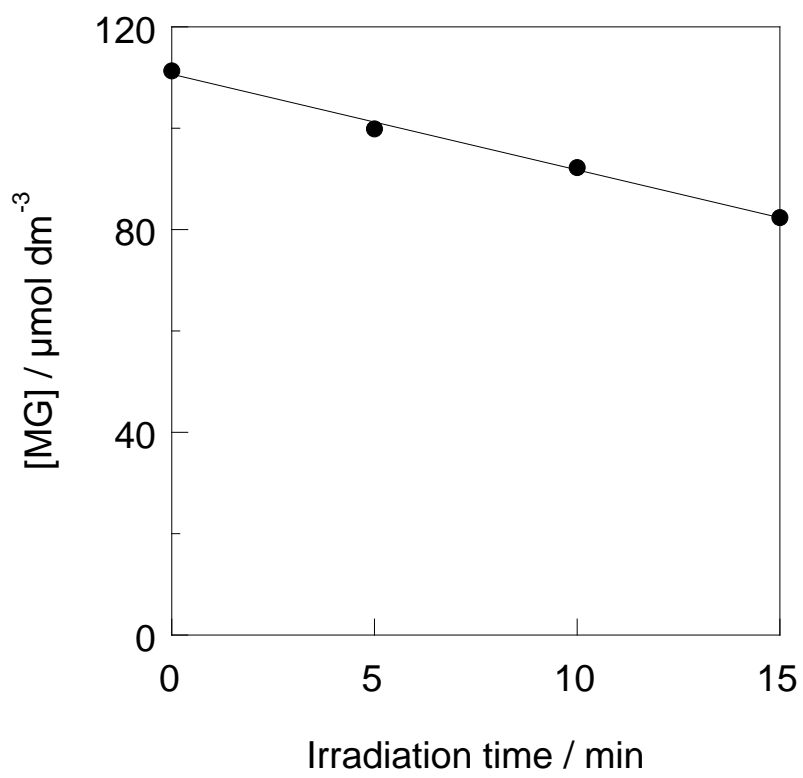
Figure 6. Time-dependency of MG concentration (circles) and TOC (squares) in the liquid phase and the amount of CO₂ (triangles) in the gas phase for HyCOM(1073) (a) and P-25 (b).



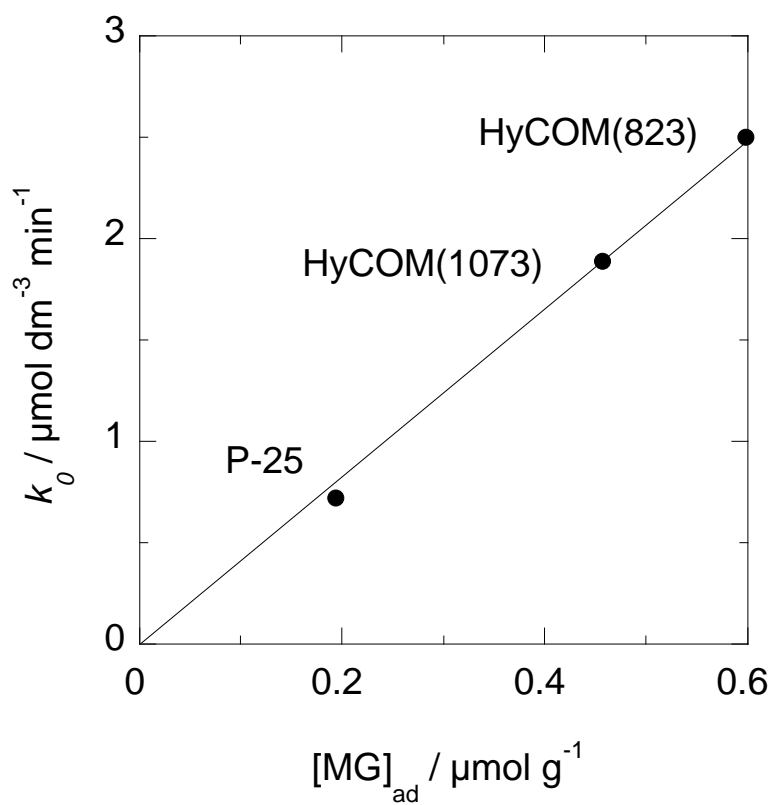
Kominami et al., Fig. 1



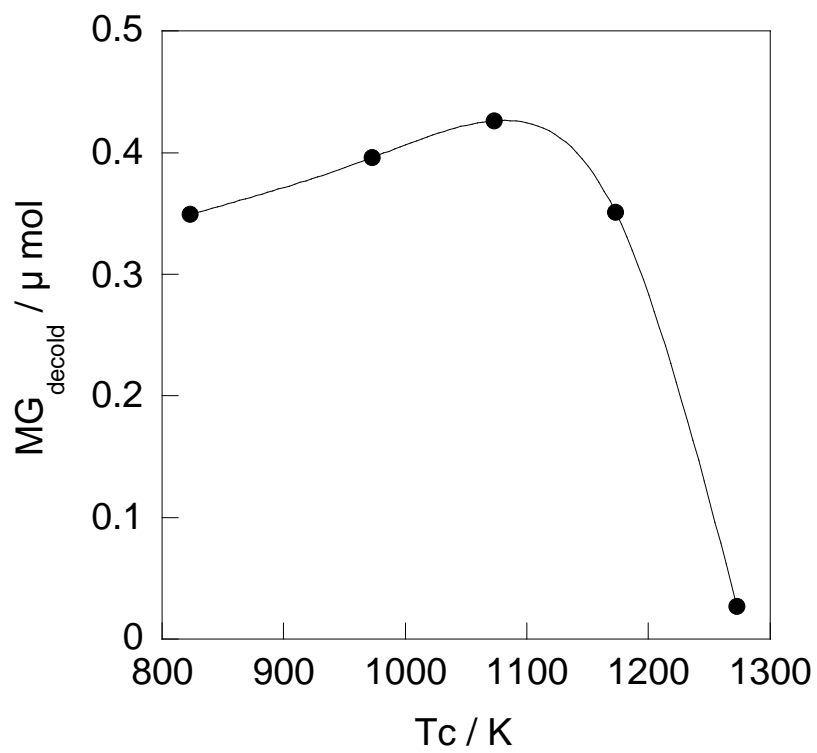
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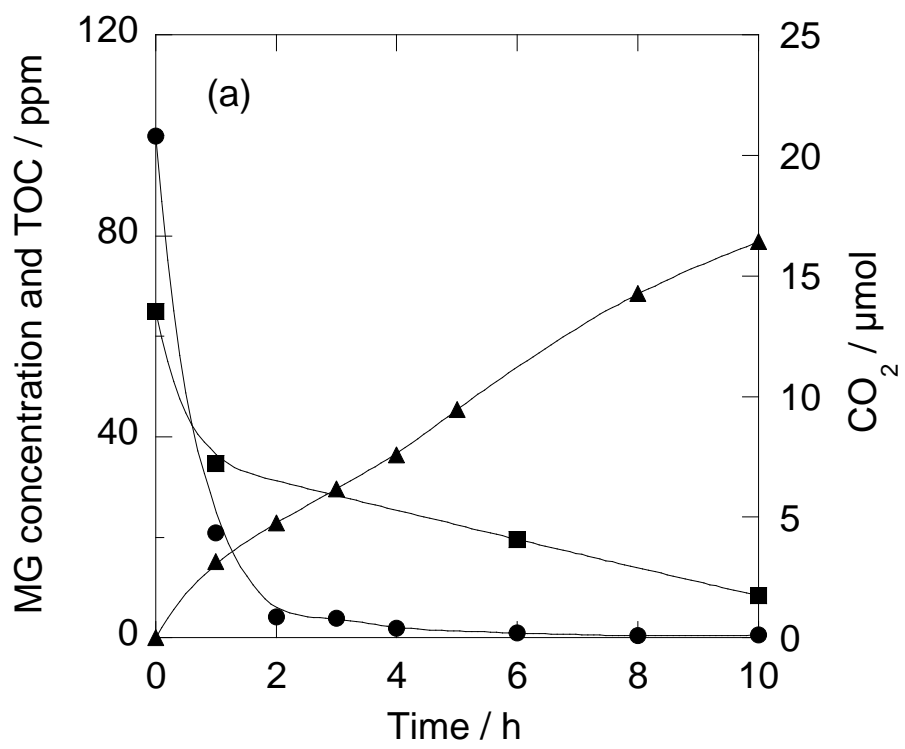
Kominami et al., Fig. 3

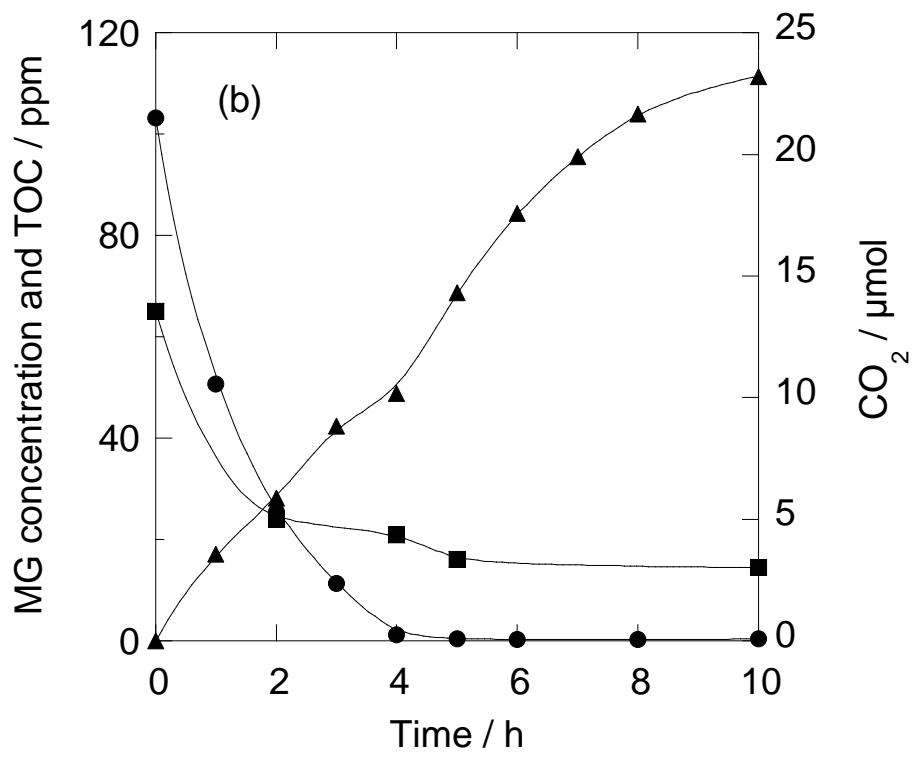


Kominami et al., Fig. 4



Kominami et al., Fig. 5





Kominami et al., Fig. 6

Table 1 Physical properties of TiO₂ powders

TiO ₂ ^a	TiO ₂ phase ^b	d ₁₀₁ ^c /nm	S _{BET} ^d /m ² g ⁻¹
HyCOM(823)	A	19	71
HyCOM(973)	A	25	36
HyCOM(1073)	A,R	47	11
HyCOM(1173)	R, A	57	5.2
HyCOM(1273)	R, A	ND	1.5
P-25	A,R	25	50

a) Calcination temperature is shown in parenthesis

b) A: anatase, R: rutile

c) Crystallite size calculated from the 101 peak of anatase

d) BET surface area

Table 2 Apparent rate constant for decolorization of malachiete green

TiO ₂	$k_0/\mu\text{mol dm}^{-3} \text{min}^{-1}$
HyCOM(823)	2.50
HyCOM(1073)	1.89
P-25	0.72

Table 3 Analysis of carbon after 10 h-irradiation

	HyCOM(1073)	P-25
TOC ^a /μg	32	62
TIC ^b /μg	53	10
Carbon as CO ₂ ^c /μg	197	279
Total carbon/μg	282	351

- a) Total organic carbon in liquid phase
- b) Total inorganic carbon in liquid phase
- c) CO₂ in gas phase