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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 (TiO_2) 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 TiO_2 ($[MG]_{ad}$) increased as the surface area of HyCOM TiO_2 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 TiO_2 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 TiO_2 with improved crystallinity continuously decreased whereas TOC in Degussa P-25 TiO_2 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 TiO_2 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 TiO_2 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 TiO_2-based photocatalysts [7,8]. Anderson and Bard [7] prepared TiO_2–SiO_2 composite photocatalysts and used them for decomposition of rhodamine-6G (R6G). SiO_2 possesses greater ability to adsorb R6G, the TiO_2–SiO_2 composite photocatalysts exhibited a higher level of decomposition activity than that of P-25 TiO_2. However, the effects of the properties of TiO_2 itself are unclear.

We have reported that nano-crystalline TiO_2 can be synthesized by the hydrothermal crystallization in organic media (HyCOM) 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

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correlations between physical properties and photocatalytic activities of HyCOM TiO_2 in several reaction systems and have found that the crystallinity of TiO_2 influenced the activity in different ways depending on the type of photocatalytic reaction [11–15]. In oxygen (O_2) evolution from an aqueous suspension of TiO_2 powders, TiO_2 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 TiO_2 suspension, TiO_2 powders with larger surface areas, i.e., higher adsorptivity, showed a higher rate of carbon dioxide (CO_2) formation, indicating that adsorption of acetic acid is important in this system [12]. Once one hole reacts with acetic acid adsorbed on TiO_2 surface, successive oxidation by O_2 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 TiO_2 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 TiO_2 were investigated.

2. Experiment

2.1. Synthesis and characterization of HyCOM TiO_2 powders

HyCOM TiO_2 powders were synthesized according to the procedure previously reported [10–15]. Titanium(IV) butoxide (Kanto Chemical, Tokyo, Japan) was dissolved in toluene (70 cm^3) in a test tube, and the test tube was then set in a 200 cm^3 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 cm^3 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 Cu Kα 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 μmol) solution (108 μmol dm^{-3}) and photoirradiated at a wavelength of >300 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, $[MG]_{ad}$, 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 TiO_2 samples and adsorption of MG

Fig. 1 shows the XRD patterns of HyCOM TiO_2 samples obtained by calcination of as-synthesized HyCOM TiO_2 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 T_c. Therefore, TiO_2 samples with various physical properties were obtained by calcination of as-synthesized HyCOM TiO_2. Thus-obtained TiO_2 samples were used for adsorption experiments and photocatalytic reactions.

Fig. 2 shows the effects of T_c on $[MG]_{ad}$ of HyCOM TiO_2 samples. HyCOM(823), which had the largest S_{BET}, showed the largest $[MG]_{ad}$ (0.60 μmol g^{-1}). Further increase in T_c resulted in monotonic decrease in $[MG]_{ad}$. However, a linear

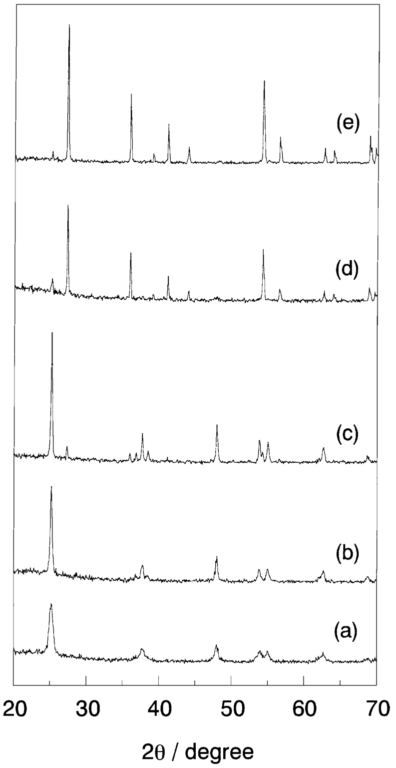

Fig. 1. XRD patterns of HyCOM TiO_2 samples obtained by calcination of as-synthesized HyCOM TiO_2 at 823 K (a), 973 K (b), 1073 K (c), 1173 K (d) and 1273 K (e).

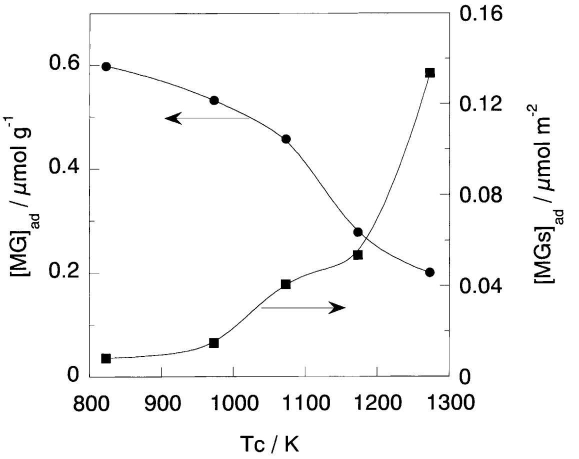

Fig. 2. T_c-dependency of the amount of MG adsorbed per unit weight ($[MG]_{ad}$) and per unit surface area ($[MGs]_{ad}$) of HyCOM TiO_2.

correlation was not observed between S_{BET} and $[MG]_{ad}$ of HyCOM TiO_2 samples, in contrast to results previously obtained for adsorption of acetic acid [15] and silver ion (Ag^+) [13,15] on HyCOM TiO_2 samples, indicating that the adsorption behavior of MG is complex compared with the adsorption behavior of simple molecules and small ions. Fig. 2 also shows the effect of T_c on the amount of MG adsorbed per unit surface area of HyCOM TiO_2 ($[MGs]_{ad}$). As expected from the non-linearity between S_{BET} and $[MG]_{ad}$, $[MGs]_{ad}$ was not constant, and $[MGs]_{ad}$ increased with elevation in T_c, 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 nm^2 molecule^{-1} based on the assumption that an MG molecule is circular and has a diameter of 1.42 nm. The value, 0.39 μmol m^{-2}, calculated from the equation $1/(A \times S_{MG})$, where A is the Avogadro's constant, means the maximal $[MGs]_{ad}$ when MG molecules horizontally adsorb to the surface of TiO_2. This value is larger than $[MGs]_{ad}$ experimentally obtained for all HyCOM TiO_2 samples, indicating that MG adsorbed horizontally to the surface of TiO_2. $[MG]_{ad}$ and $[MGs]_{ad}$ for Degussa P-25 TiO_2 were determined to be 0.193 μmol g^{-1} and 0.0039 μmol 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 μmol, which is 5.6% of the amount of MG in the starting solution (0.54 μmol). 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.

Table 1
Physical properties of TiO_2 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.

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 Fig. 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

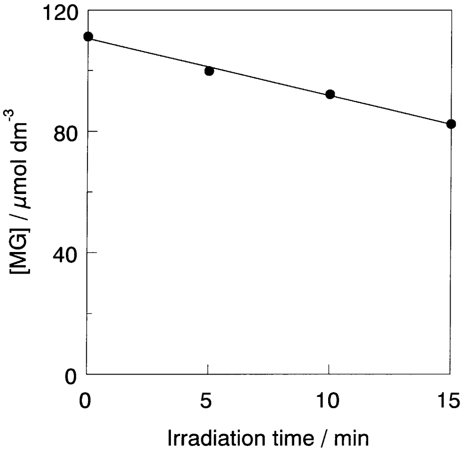

Fig. 3. Time-dependency of MG concentration in an aqueous suspension of HyCOM(1073) in the initial 15 min of irradiation.

Table 2
Apparent rate constant for decolorization of MG

TiO_2	k_0 (μmol dm^{-3} min^{-1})
HyCOM(823)	2.50
HyCOM(1073)	1.89
P-25	0.72

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 Fig. 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 $[MG]_{ad}$.

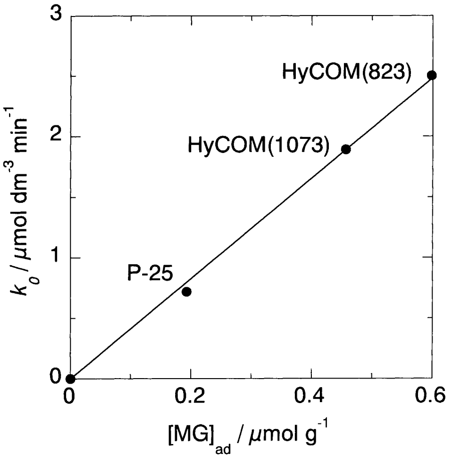

Fig. 4. Correlation between k_0 and $[MG]_{ad}$.

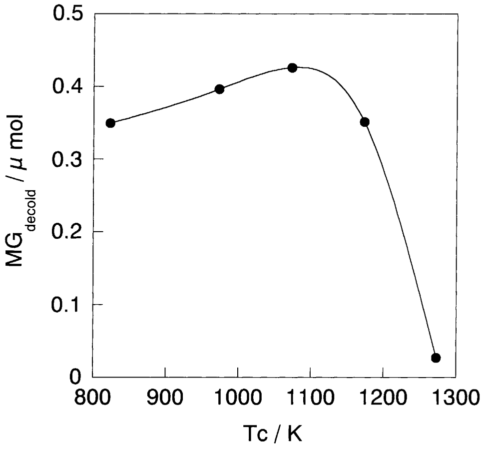

Fig. 5. T_c-dependency of MG decolored after 1 h of irradiation (MG_{decold}).

3.3. MG decomposition with prolonged irradiation

The amount of MG decolored after 1 h of irradiation (MG_{decold}), calculated from the decrease in concentration of MG in an aqueous suspension of HyCOM TiO_2, is shown in Fig. 5. MG_{decold} increased with increase in T_c and reached a maximum by calcination at 1073 K. Further increase in T_c resulted in a decrease in MG_{decold}. However, all HyCOM samples except for HyCOM(1273) decolored 60–80% of MG within only 1 h. Comparison with MG_{decold} for P-25 TiO_2 (0.266 μmol) 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 T_c-dependency of MG_{decold} was different from that of the initial decolorization, i.e., k_0. HyCOM(823) showed a larger k_0 but a smaller MG_{decold} than those of HyCOM(1073), indicating that HyCOM(823) is deactivated in an early stage. Deposit of an intermediate 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 TiO_2 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 CO_2 in the gas phase with elapse of irradiation time are shown in Fig. 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

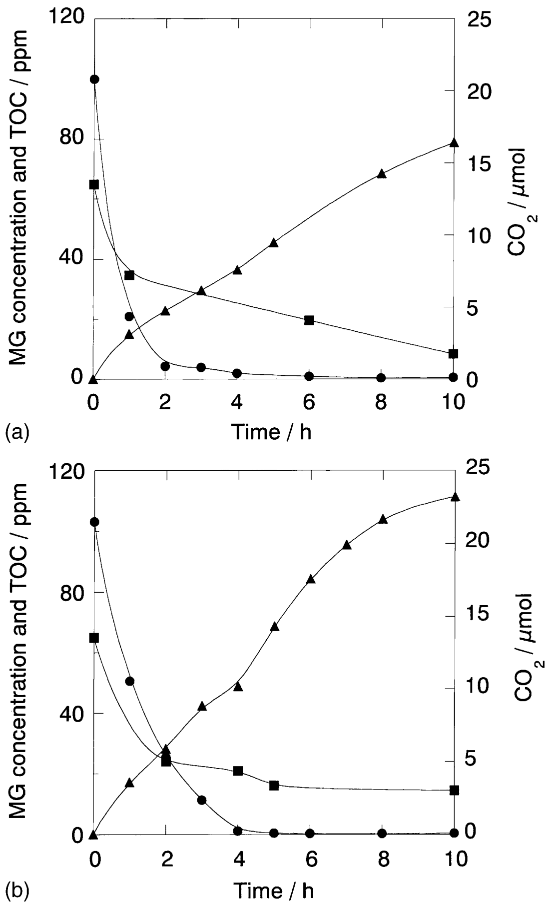

Fig. 6. Time-dependency of MG concentration (circles) and TOC (squares) in the liquid phase and the amount of CO_2 (triangles) in the gas phase for HyCOM(1073) (a) and P-25 (b).

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 decolored 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 CO_2, which is a final decomposition product, gradually increased with prolongation of irradiation time in both TiO_2 samples. The CO_2 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 CO_2 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 CO_2.

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
TC (μg)	282	351

[a] Total organic carbon in liquid phase.
[b] Total inorganic carbon in liquid phase.
[c] CO_2 in gas phase.

4. Conclusions

HyCOM TiO_2 samples with various physical properties were prepared and used for photocatalytic decomposition of MG in an aqueous solution under aerated conditions. HyCOM TiO_2 samples exhibited higher level of activity than did a commercial P-25 TiO_2 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 TiO_2 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 TiO_2 surface and that a high degree of crystallinity is required for continuous decomposition of MG into CO_2. 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 TiO_2 photocatalysts in detail and methods for regenerating deactivated photocatalysts.

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