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Titanium(IV) oxide photocatalyst of ultra-high activity: a new preparation process allowing compatibility of high adsorptivity and low electron–hole recombination probability

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Microcrystalline anatase titanium(IV) oxide (TiO_2) particles were synthesized by hydrothermal crystallization in organic media (HyCOM) followed by calcination, and used in a photocatalytic reaction system of silver metal deposition. Upon elevating the post-calcination temperature, the photocatalytic activity was enhanced in spite of the simultaneous decrease in amount of surface-adsorbed Ag^+. Comparison with the effect of calcination temperature on the other reaction systems revealed that the annealing effect became more significant with increasing number of electrons (or holes) required to complete the photocatalytic reaction process.

Keywords: titanium oxide, photocatalyst, silver metal deposition, recombination

1. Introduction

We have developed novel methods for the synthesis of several metal oxides in non-aqueous media [1–3]. These methods have the advantage that the products consist of microcrystalline particles but are sufficiently crystallized in the course of the preparation process to result in high thermal stability; they still retain large surface areas after post-calcination at even higher temperatures. Among metal oxides, titanium(IV) oxide (TiO_2) is one of the promising materials for a photocatalyst and we have reported that TiO_2 particles of average diameter ca. 10 nm are also feasibly synthesized by high-temperature hydrolysis of titanium(IV) alkoxides in organic solvents with a small amount of water dissolved from gas phase (HyCOM: hydrothermal crystallization in organic media) [1]. Although the high thermal stability is not a requisite for a semiconductor photocatalyst, well crystallized small TiO_2 particles are predicted to be highly photoactive [4]. As expected, HyCOM TiO_2 exhibited photocatalytic activities much higher than a representative active TiO_2 catalyst, Degussa P-25, for dehydrogenation of 2-propanol [5], silver metal deposition [5], N-cyclization of (S)-lysine [6] under deaerated conditions, as well as mineralization of acetic acid in aqueous solutions under aerated conditions [7]. These successful results are assumably caused by the characteristics of HyCOM TiO_2 particles; a large surface area to adsorb a large amount of substrates and the high crystallinity, i.e., less defects, to prevent the recombination of photoexcited electrons (e^-) and positive holes (h^+). In this paper, quantitative characterization of physical properties of HyCOM is discussed in relation with the photocatalytic activities toward a model system of silver metal deposition. We chose this model system because the reaction has been well characterized so far [4,8–13] and the amount of silver ions (Ag^+) adsorbed on TiO_2 surfaces ($[Ag^+]_{ads}$) can be measured precisely under conditions similar to the photocatalytic reaction. Comparison with the results of Degussa P-25 and effect of post-calcination are shown to discuss the reason for high photocatalytic activity of HyCOM.

2. Experiments

The HyCOM TiO_2 was synthesized by a procedure reported previously [1]; titanium(IV) butoxide (25 g) in toluene (70 cm^3) was heated at 573 K for 2 h in an autoclave in the presence of water (10 cm^3) fed in a space separated from the alkoxide solution. The resulting powder was washed with acetone repeatedly and dried in air at ambient temperature. As-prepared HyCOM was calcined in a furnace at various temperatures under a flow of air (30 $cm^3\,min^{-1}$); the sample was heated to the desired temperature at the rate of 10 $K\,min^{-1}$, kept at that temperature for 1 h, and cooled to room temperature. The thus calcined sample is designated by HyCOM(the calcination temperature), e.g., the sample calcined at 973 K as HyCOM(973).

TiO_2 powder was suspended in 0.5–25 $mmol\,dm^{-3}$ silver sulfate (Ag_2SO_4) aqueous solution (5.0 cm^3) in a glass tube, purged with Ar for at least 30 min, and then sealed off with a rubber stopper. The suspension was photoirradiated with a 400 W high-pressure mercury arc at 298 K under magnetic stirring (1000 rpm). After the irradiation, the amount of evolved oxygen (O_2) was measured by a gas chromatograph. The catalyst was centrifuged, washed repeatedly with distilled water, and dried overnight at 353 K.

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The photodeposited Ag was dissolved with concentrated HNO_3 and measured by inductively coupled plasma (ICP) emission spectroscopy (Shimadzu ICPS-1000III). The Ag^+ adsorption, $[Ag^+]_{ads}$, in the dark was measured under conditions similar to the photocatalytic reaction by ICP from the difference in Ag^+ concentration before and after addition of TiO_2 into Ag_2SO_4 solutions of various concentrations.

3. Results and discussion

Figure 1 shows $[Ag^+]_{ads}$ of HyCOM(973) and P-25 as a function of equilibrium concentration of Ag^+ ($[Ag^+]_{eq}$). Both TiO_2's gave Langmuirian isotherms. From the linear double-reciprocal plots, a limiting amount of Ag^+ adsorption of 109 and 192 μmol g^{-1}, and an adsorption equilibrium constant of 210 and 205 mol^{-1} dm^3 were evaluated for HyCOM(973) and P-25, respectively. A similar equilibrium constant (440 mol^{-1} dm^3) has been reported for a commercial anatase powder (Merck) [8]. The ratio of limiting adsorption, ca. 1.8, is attributable to that in specific (BET) surface area (34 and 50 m^2 g^{-1}) [14], ca. 1.5, suggesting that the density of adsorption sites on the TiO_2 surface is independent of the preparation process. The almost similar equilibrium constant also supports this.

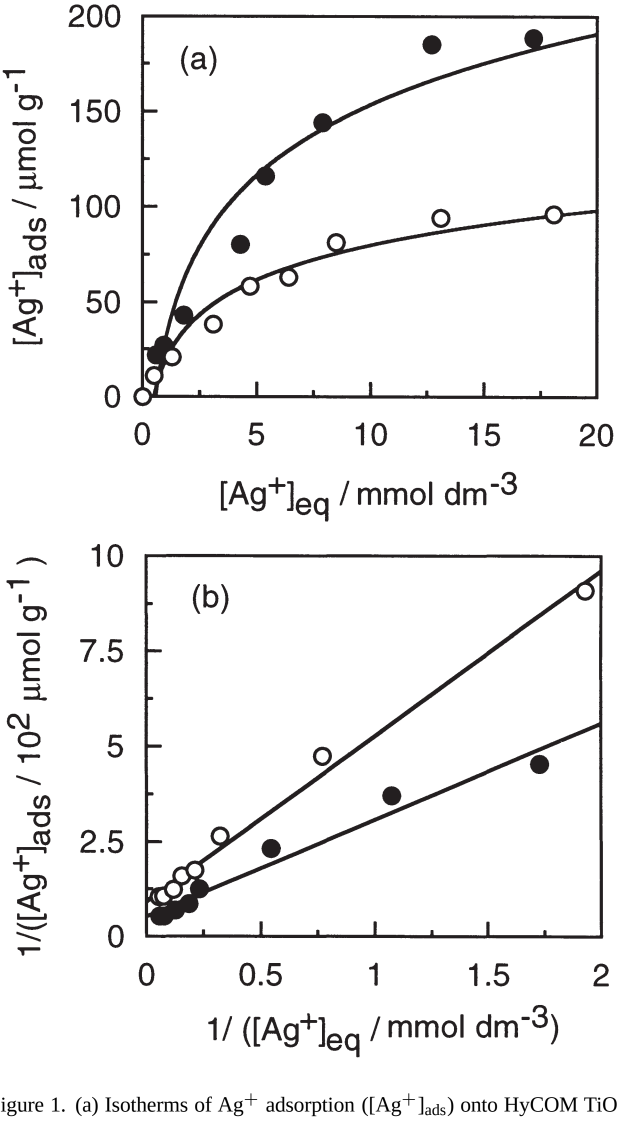

Figure 1. (a) Isotherms of Ag^+ adsorption ($[Ag^+]_{ads}$) onto HyCOM TiO_2 calcined at 973 K (HyCOM(973)) (○) and Degussa P-25 (●). (b) Double reciprocal Langmuirian plots of data shown in (a).

Photoirradiation onto the TiO_2 particles suspended in an aqueous Ag_2SO_4 solution led to the liberation of O_2 in the gas phase together with deposition of Ag metal on the TiO_2 surface. The product yields satisfied the stoichiometry of this reaction, $4Ag^+ + 2H_2O \rightleftharpoons 4Ag + O_2 + 4H^+$, as table 1 shows.

It has been proved that pH decrease by the liberated proton causes protonation of surface hydroxyls resulting in inhibition of adsorption of cations [4,8]. To avoid the effect of change in $[Ag^+]_{ads}$ during the photoirradiation, the rate of photocatalytic reaction (R_{Ag}) was estimated from the yield of deposited Ag by short irradiation time, e.g., 5 min. Figure 2 shows the correlation between R_{Ag} and $[Ag^+]_{ads}$.

The linear relations clearly indicate that the rate is proportional to the amount of substrates adsorbed on the particles and, thereby, the adsorptivity is one of the decisive factors for reaction rate. Another important finding is that the slope for HyCOM(973) (1.3) was ca. three times larger than that for P-25 (0.45). The importance of the balance of adsorptivity and recombination probability in photocatalytic reactions has, as far as we know, been pointed out earlier by Fleischauer and co-workers [15] and recently by Martin and co-workers [16]. In the previous paper [17], we have investigated the recombination kinetics after photoexcitation of several TiO_2 powders by femtosecond pump–probe diffuse reflectance measurements and found that the second-order rate constant for e^-–h^+ recombination for HyCOM(973) was 2–2.5 times smaller than that for P-25, which is almost consistent with the ratio of the slope in this study. Of course, other possibilities controlling the reaction rate are also considered, e.g., difference in the average density of e^-–h^+ in the photoirradiated particles which might be affected by many factors such as impurity content and surface structure of TiO_2 particles although two TiO_2 powders have almost similar particle size, surface area, and crystal structure. However, as one of the most probable reasons, the low e^-–h^+ recombination probability for HyCOM(973) is attributable to the apparently large rate in spite of relatively small $[Ag^+]_{ads}$.

Table 1 shows the effect of calcination on the physical properties, $[Ag^+]_{ads}$ and R_{Ag}, of HyCOM TiO_2's. The crystallite size of anatase and the BET surface area of the as-prepared sample were 11 nm and 140 m^2 g^{-1}, respectively. With elevating the calcination temperature, the crystallite size was increased and the surface area was decreased, reflecting crystal growth and sintering of the anatase crystallites upon calcination. It should be noted that even after calcination at 973 K the sample remained in the anatase phase and had a large surface area of 34 m^2 g^{-1}. The factor of adsorptivity, $[Ag^+]_{ads}$, was also reduced by the

Table 1
Physical properties, silver ion adsorptions, and photocatalytic activities of TiO_2 powders.

TiO_2	T_{cal}[a] (K)	S_{BET} ($m^2\,g^{-1}$)	d_{101}[b] (nm)	$[Ag^+]_{ads}$ ($\mu mol\,g^{-1}$)	Ag[c] ($\mu mol\,h^{-1}$)	O_2[c] ($\mu mol\,h^{-1}$)	$Ag/4O_2$
HyCOM	–	140	11	496	10	<1	–
HyCOM	573	133	10	485	15	<1	–
HyCOM	823	78	18	368	25	5	1.36
HyCOM	973	34	26	98	108	28	0.96
HyCOM	1073	8	47	33	149	39	0.95
HyCOM	1173	3	55	18	185	46	1.00
HyCOM	1273	3	–	13	187	48	0.96
P-25	–	50	25	192	67	16	1.00
ST-01	–	300	–	900	15	4	0.85

[a] HyCOM TiO_2 powders were prepared at 573 K in toluene and calcined at T_{cal}.

[b] Crystallite size calculated from the 101 diffraction peak of anatase.

[c] Rates for photocatalytic Ag metal deposition and O_2 evolution from an aqueous Ag_2SO_4 solution (initial concentration of Ag^+ was 50 mmol dm^{-3}).

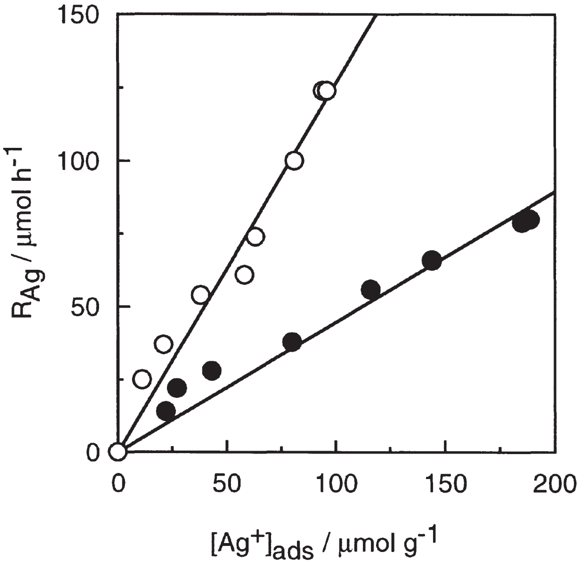

Figure 2. Correlation between the initial rate of photocatalytic Ag metal deposition (R_{Ag}) and $[Ag^+]_{ads}$ of HyCOM(973) (○) and P-25 (●).

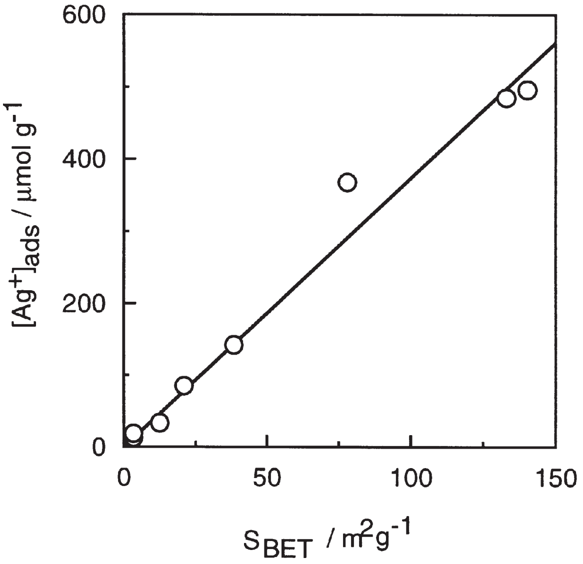

Figure 3. Plots of $[Ag^+]_{ads}$ of HyCOM TiO_2 calcined at various temperatures in air as a function of their BET surface area.

calcination (figure 4) and almost proportional to the BET surface area (figure 3).

This fact shows that the density (ca. 2.5 Ag^+-ion nm^{-2}) and property of adsorption sites on TiO_2 is independent of the crystallite size and/or surface area, i.e., the adsorption characteristic and reactivity of Ag^+ toward e^- is kept constant upon calcination.

If the properties of crystal bulk, e.g, rate of e^-–h^+ recombination, are not influenced by the calcination, a decrease in photocatalytic reaction rate by calcination is expected from the above-mentioned behavior of $[Ag^+]_{ads}$. However, on the contrary, the apparent rate of photocatalytic Ag deposition was enhanced by the higher-temperature calcination, as figure 4 shows. Similar results for this reaction were observed in commercial TiO_2's [11] and TiO_2 samples prepared by hydrolysis of titanium isopropoxide [10,12], although the rate was decreased upon severer calcination at 973–1173 K. Effect of calcination on the recombination rate for HyCOM TiO_2 was also exam-

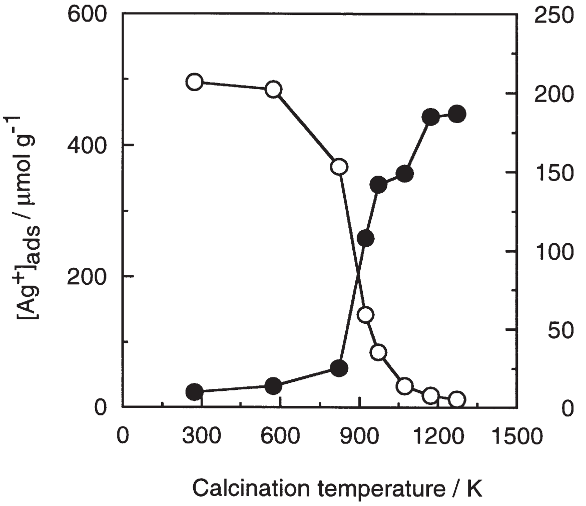

Figure 4. Effect of calcination on $[Ag^+]_{ads}$ (○) and R_{Ag} (●) of HyCOM TiO_2.

ined by the femtosecond pump–probe diffuse reflectance measurement and the rate drastically decreased upon calcination [17]. This supports that one possible explanation for the increase in the photocatalytic reaction rate is reduced probability of e^-–h^+ recombination due to annealing of crystallites. The calcination improves the crystallinity and reduces crystal defects, which should predominantly act as recombination centers for e^-–h^+, leading to smaller probability of the recombination and enhanced photocatalytic activity. Since, as reported previously [5], the quantum efficiency of the photocatalytic reaction by HyCOM was estimated to be ca. 30% and, thereby, a large part of e^-–h^+ undergoes mutual recombination, such effect of calcination to diminish the recombination seems to be reasonable.

A similar effect of high-temperature calcination of rutile TiO_2 powder has been reported by Oosawa and Grätzel [11]. They attributed the calcination-induced enhancement of photocatalytic activity for Ag deposition along with O_2 evolution to a decrease in surface-hydroxyl density, though the role of surface hydroxyls seemed not to be clarified. Sato and Kadowaki pointed out that there are many factors influencing the overall reaction rate [12,13], e.g., reduction of powders enhances the Ag deposition rate due to increase in conductivity in the particle [13]. Although there still remains a possibility that another factor such as surface hydroxyl density, oxygen vacancies, conductivity, light scattering characteristics or steady-state density of e^-–h^+ in each particle affects the overall reaction rate, our hypothesis seems to be consistent with the results of the other photocatalytic reaction systems.

Our recent papers have shown the effect of calcination temperature on photocatalytic activities of HyCOM for mineralization of acetic acid under aerated condition [7] and dehydrogenation of 2-propanol under deaerated condition [5]. Although, unfortunately, the relatively higher detection limits did not allow us to determine the amount of adsorbed substrates under conditions similar to those of the photocatalytic reaction, it could be assumed that the amount of adsorbed substrates is proportional to the specific surface area, as seen in figure 3. In the former system, the as-prepared HyCOM showed the highest activity and the activity was monotonously decreased with elevating calcination temperature, i.e., decreasing surface area; the adsorptivity factor predominates in this case. Being compatible with these results, a commercial TiO_2, Ishihara ST-01, having large BET surface area but showing lower activity for Ag deposition (table 1), exhibited higher photocatalytic activity. In the latter system, the activity was increased with calcination up to 973 K and decreased at the higher temperature. Since, in this case, transformation of crystallites from anatase into rutile might affect the ability of TiO_2 particles [10], the interpretation of overall rate is a little complicated. But, in the region where crystallites were anatase, a predominant effect of the calcination rather than the adsorptivity was clearly seen. While this tendency is similar to the present Ag-deposition system, it should be noted that the as-prepared HyCOM showed moderate, but not negligible, activity. Thus, the calcination influenced the photocatalytic activity in a different way depending on the type of reactions.

Such behavior seems to be related to the difference in number of electrons (or holes) required to complete the photocatalytic reactions; the larger the number becomes, the more the recombination probability affects. For mineralization of acetic acid, one can expect that the reaction proceeds spontaneously after one-electron (hole) oxidation of the substrate acetic acid, since a proposed intermediate radical undergoes addition of O_2 followed by thermal degradation [18]. The dehydrogenation of 2-propanol is formally a two-electron process. Being different from these reactions, completing the Ag deposition together with O_2 evolution requires four electrons. In other words, four holes must migrate in the particle, escaping from the recombination, before arriving at the site for O_2 evolution. It seems that, under these circumstances, the recombination becomes a more significant factor determining the photocatalytic activity. TiO_2 powders as prepared or calcined at lower temperature adsorb large amounts of substrates but, assumably due to their crystal defects, migration of active species may be markedly prohibited. On the contrary, HyCOM calcined at the higher temperature or P-25, which is prepared via high-temperature gas-phase process, exhibits superior photocatalytic activity, especially when the reaction needs a multiple number of electrons (holes).

Being consistent with the above arguments, we could see improvement of photocatalytic activity of HyCOM calcined at a middle temperature range between 823 and 1073 K by adding 2-propanol (0.5 mmol) to the starting Ag_2SO_4 solution (figure 5), e.g., the rates for Ag metal deposition together with acetone formation ($2Ag^+ + CH_3CHOHCH_3 \rightleftharpoons 2Ag + CH_3COCH_3 + 2H^+$) [19] by HyCOM(823) and HyCOM(1073) were increased from 25 and 149 to 60 and 245 $\mu mol\,h^{-1}$, respectively. Essentially the same behavior has been reported earlier for TiO_2 powders prepared from

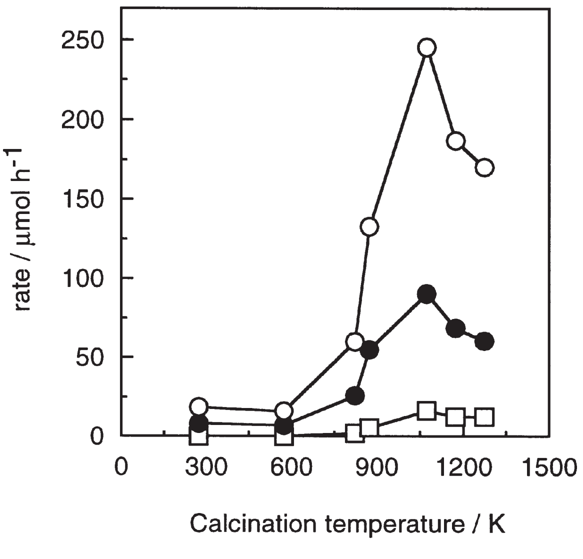

Figure 5. Effect of calcination on the rate of photocatalytic reaction (Ag (○), acetone (●), and O_2 (□)) in an aqueous Ag_2SO_4 solution (25 $mmol\,dm^{-3}$) in the presence of 2-propanol (0.5 mmol).

alkoxide [10]. This may be accounted for by the change in number of electrons from 4 (O_2) to 2 (acetone).

4. Conclusion

A highly active TiO_2 photocatalyst has been synthesized by the newly developed HyCOM method followed by calcination in air. Comparison with the representative commercial TiO_2 catalyst, Degussa P-25, revealed that HyCOM had a little less adsorptivity toward Ag^+ ions, but its electron–hole recombination probability might be ca. three times smaller than for P-25 judging from the amount of adsorbed substrate. The low recombination probability for HyCOM was consistent with the result directly observed with the femtosecond pump–probe diffuse reflectance measurement. Two significant factors for active photocatalysts, adsorptivity and recombination probability, are well balanced in HyCOM, which is probably attributed to the higher photocatalytic reaction rate. Effects of post-calcination temperature on several photocatalytic reactions were studied and their difference could be interpreted reasonably by taking the number of electrons (or holes) to complete the photocatalytic reaction into account. For the reactions proceeding via one-electron transfer, e.g., oxidation of organic compounds under aerated conditions, high adsorptivity is a major factor, while for those of multi-electron processes, e.g., those accompanying O_2 evolution, a low recombination probability seems to be desirable. This is the first report, to the best of our knowledge, showing a strategy for syntheses of the most suitable photocatalysts toward different reaction systems.

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