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Photoacoustic spectroscopic estimation of electron mobility in titanium(IV) oxide photocatalysts

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Abstract

Double-beam photoacoustic (PA) spectroscopy was employed in measurements on the decay of trivalent titanium (Ti^{3+}) species, in titanium(IV) oxide (TiO_2) photocatalysts, produced by trapping of photoexcited electrons. The PA signal attributed to Ti^{3+} rapidly decayed in the dark due to the electron transfer from Ti^{3+} to molecular oxygen (O_2) adsorbed on the surface. The rate of decay was evaluated for various TiO_2 powders by the analysis of decay profile, and compared with the rate of photocatalytic dehydrogenation of methanol in an aqueous solution. The observed positive correlation between them suggests that both decay of Ti^{3+} by O_2 and photocatalytic dehydrogenation of methanol are governed by the mobility of photoexcited electrons.

1. INTRODUCTION

Photocatalysis over semiconductors involves the absorption of light of energy larger than their band gap, generating excited electron (e^-) and positive hole (h^+), and subsequent reduction and oxidation by e^- and h^+ , respectively. Many redox reactions have been proved to proceed by photocatalysis. However, the detailed mechanism, e.g., how e^- and h^+ , produced in the bulk of photocatalyst, move to the surface to react with adsorbed substrates, is still ambiguous. One of the most probable mechanisms of e^- migration in the photocatalyst is migration in conduction band as well as hopping via electron-trapping sites and the trapped e^- could be detected and quantitatively measured as trivalent titanium species (Ti^{3+}) [1]. Tracing of Ti^{3+} , therefore, during the TiO_2 -induced photocatalytic reactions would provide the mechanistic information. The conventional methods for Ti^{3+} detection were, however, not suitable for *in situ* measurements, e.g., a photochemical method using methyl viologen requires filtration of photocatalyst particles and an ESR method does removal of O_2 in the system. Photoabsorption spectroscopy would be an

alternative method when an ultrafast pulse laser was used as excitation light source [2], but, generally speaking, such less intense photoabsorption by Ti^{3+} can not be detected under photoirradiation in usual photocatalytic reaction systems. Recently, we have developed a double-beam photoacoustic (PA) spectroscopic technique for *in situ* detection of Ti^{3+} and reported that PA measurement under continuous ultraviolet (UV) light irradiation enable the *in situ* estimation of saturation limit of molar amount of Ti^{3+} in TiO_2 samples under the conditions similar to ordinary photocatalytic reaction systems [3]. In this paper, using 21 TiO_2 powders, decay of Ti^{3+} in the dark was investigated to elucidate the mobility of electrons which may be correlated with photocatalytic activity of each photocatalyst.

2. EXPERIMENTAL

2.1. Samples

Twenty-one TiO_2 powders supplied from commercial sources (Merck and Showa Titanium ST series) and Catalysis Society of Japan as reference catalysts (JRC-TIO series) were used. Their crystal structure was determined by powder X-ray diffraction analysis and specific surface area (S_{BET}) was measured by nitrogen adsorption on the basis of the Brunauer-Emmett-Teller equation.

2.2. Double-beam photoacoustic spectroscopy

A home-made PA cell composed of an aluminum body (inside volume, ca. 1 cm^3), a Pyrex window and two valves for gas flow was used. A powder sample was placed in the cell and the atmosphere was controlled by the flow of O_2 containing methanol vapor. The measurements were conducted in the closed system at room temperature. The light source was a light-emitting diode (LED; Luxeon LXHL-NM98, emitting around 645 nm) and its output intensity was modulated by a digital function generator (NF DF1905). PA signal acquired by a condenser microphone buried in the cell was amplified and monitored by a digital lock-in amplifier (NF LI5640). In addition to the modulated light, a UV-LED (Nichia NCCU033, emitting around 365 nm) was also used as a simultaneous continuous irradiation (0.11 mW cm^{-2}) for excitation of TiO_2 .

2.3. Photocatalytic reaction

An aqueous suspension composed of 50 mg of TiO_2 and 5 cm^3 of a methanol solution (50 vol%) containing hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), the amount of which corresponds to 2-wt% loading of platinum (Pt), were photoirradiated under an argon atmosphere with magnetic stirring (1000 rpm). Gaseous product, hydrogen (H_2), was analyzed by gas chromatography (Shimadzu GC-8A equipped with a molecular sieve 5A column and a TCD).

3. RESULTS AND DISCUSSION

Figure 1 shows time-course curves of PA signal for three representative TiO_2 samples. The samples were exposed to UV light for initial 30 min and then kept in the dark. In all case, the PA

intensity increased by UV irradiation and then became almost saturated. The increase is attributable to accumulation of Ti^{3+} , which has broad absorption in visible region, by capture of e^- in the trapping sites as a counter part of hole consumption with methanol and simultaneous electron transfer from Ti^{3+} to surface-adsorbed O_2 [3]. Analysis of this UV-induced rise enabled estimation of saturation limit of Ti^{3+} accumulation, reflecting the nature of TiO_2 powders, but is not discussed here.

After UV turn-off, the PA intensity rapidly decreased as Fig. 1 shows, the rate of which depended on the samples. Since the rate was much lower in the absence of O_2 , the decay in PA signal is attributed to the consumption of Ti^{3+} through the electron transfer from Ti^{3+} to O_2 adsorbed on TiO_2 . Fitting these curves to a first-order (single-exponential) or second-order kinetic equation was failed suggesting the heterogeneity of location (surface or bulk) and energy level of Ti^{3+} and/or O_2 . The curves were, therefore, fitted for convenience to a set of two exponential functions I (eq. (1)) and the weighted mean rate constant (k_{wm}) was calculated from their components (eq. (2)).

$$I(t) = \sum_{i=1}^2 a_i \exp(-k_i t) \quad (1) \quad k_{wm} = \frac{\sum_{i=1}^2 a_i k_i}{\sum_{i=1}^2 a_i} \quad (2)$$

Figure 2 shows plots of k_{wm} against S_{BET} . A tendency of increasing k_{wm} along with the increase in S_{BET} was observed only for anatase-rich samples, but in overall there seems to be no appreciable correlation between them. Although at present we have no proof, the rate of Ti^{3+} decay is most probably governed by the mobility of e^- in the TiO_2 particles; the mobility might be high if e^- migrates in conduction band without being trapped by the sites of energy lower than the bottom of conduction-band. The particle size may also give influence on the e^- mobility; migration path length should be shorter when the size is small. Therefore, it is reasonable not to obtain appreciable correlation between k_{wm} and S_{BET} on the assumption that the e^- mobility is reflected on k_{wm} .

In Fig. 3 are plotted the photocatalytic activity, r , which was evaluated by H_2 liberation from aqueous methanol solutions, against k_{wm} . For TiO_2 of $k_{wm} < 10^{-1} \text{ s}^{-1}$, positive correlation between r and k_{wm} was observed, indicating significant contribution of Ti^{3+} reactivity to the photocatalytic activity. It should be noted here that the Pt-deposited TiO_2 was used in the photocatalytic reaction, while bare TiO_2 was used in the PA measurement. In the absence of Pt, as has been observed in the PA measurement [3], e^- is accumulated in the form of Ti^{3+} , while it is well known that the Pt deposits accelerates the reaction of e^- with proton or water to liberate H_2 . Thus, the correlation of Ti^{3+} reactivity reflecting k_{wm} with r can be rationalized by assuming the intermediacy of Ti^{3+} . Another possible interpretation is that both r and k_{wm} are influenced, at least, by the density of trapping sites both retarding the e^- migration in the dark in the absence of h^+ and enhancing the recombination of e^- and h^+ by trapping. At higher $k_{wm} > 10^{-1} \text{ s}^{-1}$, r was almost

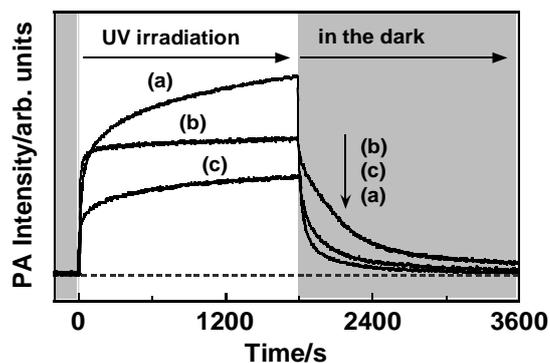


Fig. 1 Time-course curves of PA signal of (a) JRC-TIO-11, (b) JRC-TIO-1, and (c) JRC-TIO-2.

saturated. Exceptions were two TiO₂ samples (JRC-TIO-3 and 6), which are pure rutile (while the others contains anatase crystallites) and exhibiting lower photocatalytic activity. Since there is a limitation of flux of photons incident on TiO₂ and of rate of diffusion of substrates, methanol and/or proton, such saturation can be reasonably accepted. Even if recombination of e⁻ and h⁺ is almost suppressed in TiO₂ of higher k_{wm} , the quantum efficiency can not exceed unity, since photocatalytic dehydrogenation of methanol in the absence of O₂ is considered to be non radical-chain reaction.

Thus, it has been proved that the empirical rate constant of decay of photoaccumulated Ti³⁺ in the dark, reflecting the reactivity of Ti³⁺ or the e⁻ mobility, is correlated with the rate of photocatalytic reaction by anatase-crystallites containing TiO₂ samples. This suggests that both e⁻ mobility and photocatalytic activity depends on the nature and density of electron trapping sites in TiO₂.

4. CONCLUSION

Analysis of 21 TiO₂ samples by double-beam (intensity-modulated visible and continuous UV) PA spectroscopy revealed that the rate of decay, in the dark, of photoaccumulated Ti³⁺ through the reaction with O₂ depended on the nature of TiO₂ and estimated empirical rate constant of decay was correlated with the photocatalytic activity. Thus, the present double-beam PA technique enabled to trace the change in visible-light photoabsorption arising by the UV photoirradiation of TiO₂ and to obtain mechanistic information on the photocatalysis.

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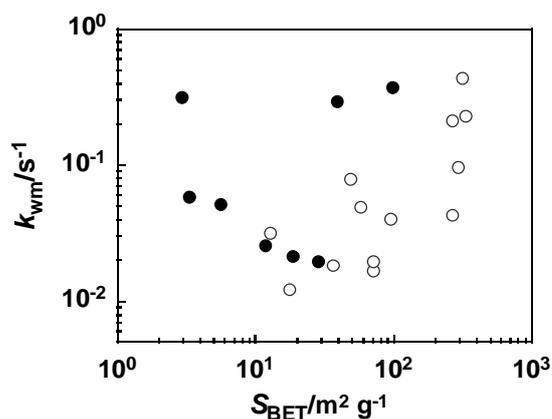


Fig. 2 Plots of k_{wm} against S_{BET} . Closed and open symbols refer to mainly rutile and anatase samples, respectively.

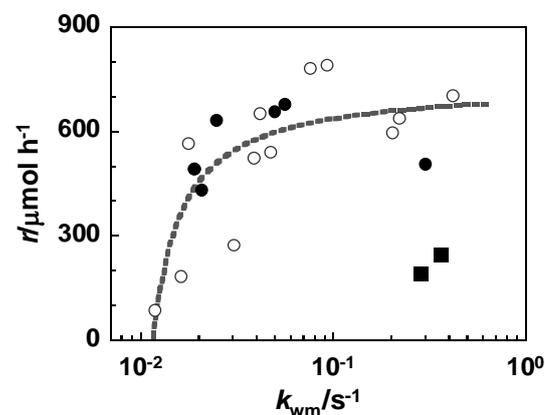


Fig. 3 Plots of r against k_{wm} . Closed and open symbols refer to mainly rutile and anatase samples, respectively. Squares show pure rutile TiO₂.