Photocatalytic activity of transition-metal-loaded titanium(IV) oxide powders suspended in aqueous solutions: Correlation with electron–hole recombination kinetics

Shigeru Ikeda,[a,b] Noboru Sugiyama,[b] Bonamali Pal,[a] Giuseppe Marcí,[c] Leonardo Palmisano,[c] Hidenori Noguchi,[d] Kohei Uosaki[d] and Bunsho Ohtani[a,b]

[a] *Catalysis Research Center, Hokkaido University, Sapporo 060-0811, Japan. E-mail: ohtani@cat.hokudai.ac.jp*
[b] *Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan*
[c] *Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Universitá di Palermo, Viale delle Scienze, 90128, Palermo, Italy*
[d] *Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan*

Received 4th October 2000, Accepted 28th November 2000
First published as an Advance Article on the web 21st December 2000

Photocatalytic reactions by transition-metal (V, Cr, Fe, Co, Cu, Mo, or W) loaded TiO_2 (M-TiO_2) powders suspended in aqueous solutions of methanol, (*S*)-lysine (Lys), or acetic acid were investigated. The photoactivities of various samples were compared with the rate constant (k_r) of recombination of photoexcited electrons and positive holes determined by femtosecond pump–probe diffuse reflection spectroscopy (PP-DRS). As a general trend, increased loading decreased the rate of formation of the main products (H_2, pipecolinic acid (PCA), and CO_2) under UV (> 300 nm) irradiation, and the effect became more intense on increasing the loading. In PP-DRS, these M-TiO_2 gave similar decays of absorption at 620 nm arising from excitation by a 310 nm pulse (< 100 fs). The second-order rate constant (k_r) markedly increased with loading, even at a low level (0.3%) and further increased with an increase in loading up to 5%. The photocatalytic activity of platinized M-TiO_2 for H_2 and PCA production under deaerated conditions depended strongly on k_r, but the relation between k_r and the rate of CO_2 production by unplatinized M-TiO_2 under aerated conditions was ambiguous; other factor(s) might control the rate of the latter. These different k_r dependences of photoactivity on the reaction kinetics governed by e^-–h^+ recombination were attributed to the presence of O_2 and Pt deposits. A simple kinetic model to explain the overall rate of these photocatalytic reactions is proposed, and the effect of recombination kinetics on photoactivity is discussed.

Introduction

Titanium(IV) oxide (TiO_2) has been investigated extensively as one of the most promising candidates for a semiconductor photocatalyst,[1] and has been found to be suitable for a wide range of processes, including solar energy conversion and storage,[2,3] reductive fixation of carbon dioxide,[4] organic synthesis,[5,6] and mineralization and/or detoxification of organic compounds.[7,8] A disadvantage of the use of TiO_2 as a photocatalyst is that it absorbs only UV light at $\lambda < 400$ nm, and therefore a significant fraction of the solar radiation is not used in TiO_2 photocatalytic reactions, though this photoabsorption property, as TiO_2 is practically white or colorless, enables us to apply photocatalytic coatings without changing the appearance of the underlying materials. In order to extend the range of photoabsorption to visible light matching the solar radiation, doping of metals, especially transition metals ions, into the TiO_2 crystal lattice or loading them on the TiO_2 surface has been shown to be successful in several studies.[9–14] The absorption spectrum has been extended to the visible region, and photoresponses, *i.e.*, visible light-induced photocatalytic reactions, on modified TiO_2 have been reported. However, it should be noted that in most cases the fundamental photocatalytic activity of TiO_2, UV light-induced band-gap excitation seemed to be reduced, in spite of the emphasis on visible-light response. As a possible explanation, some investigators have concluded that the doping or loading of metals, acting as or leading to the formation of defective sites in the crystal lattice, accelerates recombination of photoexcited electrons and positive holes.[10,12] However, this is still only speculation, and no clear evidence of an effect of transition metal on the photocatalytic activity of TiO_2 due to its band-gap excitation has yet been obtained. Furthermore, to the best of our knowledge, few detailed examinations on the correlation between the recombination rate and photocatalytic activity have been performed.

In the primary stage of the photocatalytic reaction, the band-gap photoabsorption of TiO_2 generates photoexcited electrons and holes, which can migrate to the surface to drive redox reactions with adsorbed substrates, competing with their disappearance due to mutual recombination. Although the mechanism and/or kinetics of such fast primary events in heterogeneous systems have been poorly understood so far, mainly due to the limitation of time resolution in conventional techniques, recent progress in laser technology has enabled direct measurement of the dynamics of heterogeneous electron transfer with a time resolution even faster than 100 fs.[15–26] For TiO_2 particles and colloids,[20–26] femtosecond PP transient absorption spectroscopy has shown that certain surface sites trap electrons within a few tens of fs after the photoexci-

DOI: 10.1039/b008028o

tation, giving a broad absorption at around 500–650 nm,[27,28] and their recombination with holes induces decay of absorption within 100 ps with second-order kinetics.[23,24] Analysis of the ultrafast absorption decay kinetics of opaque TiO_2 powders measured in a diffuse reflection mode has shown that the observed lifetime of trapped electrons is closely related to the photocatalytic activity;[24–26] the longer the lifetime of trapped electrons, the higher the photocatalytic activity of commercial and synthesized TiO_2 powders. These facts suggest that kinetic parameters, *e.g.*, the rate constant of the absorption decay, could be a significant measure of the photocatalytic activity.[24]

The purpose of this study was to apply PP-DR spectroscopy to transition-metal-loaded TiO_2 powders to clarify the influence of loaded metal on the rate of recombination of electrons and holes under UV photoirradiation. A series of TiO_2 photocatalysts with varying amounts of loaded transition metals (V, Cr, Fe, Co, Cu, Mo, or W) were used for several photocatalytic reactions: methanol dehydrogenation, conversion of (*S*)-lysine (Lys) into (*S*)-pipecolinic acid (PCA), and oxidation of acetic acid. The initial reaction rates were compared with the relative rate constants of electron–hole recombination determined using PP-DR spectroscopy.

Experimental

Materials

Bare and metal-loaded TiO_2 powders were prepared as follows: An aqueous solution of ammonia (Carlo Erba RPE, 25%) was added dropwise at 298 K to an aqueous solution of $TiCl_3$ (Carlo Erba RPE, 15%) to obtain a white precipitate, which was then dried in air at 373 K followed by calcination at 773 K for 24 h in air. The as-prepared bare TiO_2 was suspended in an aqueous solution of metal nitrates or ammonium salts of hetero polyacids ($Cr(NO_3)_3 \cdot 9H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, NH_4VO_3, $(NH_4)_6Mo_7O_{24}$, and $(NH_4)_6W_{12}O_{39}$), and then the slurry was dried and calcined at 773 K for 24 h in air. In all catalyst preparation processes, the content of metal was 0.3, 1, 2, or 5%, calculated as the molar ratio of loaded metal to the total metal, including Ti. Measurements of powder X-ray diffraction and nitrogen adsorption at 77 K showed that all the TiO_2 powders consisted mainly of well-crystallized anatase with a similar BET surface area of *ca.* 35–60 $m^2 g^{-1}$. The detailed characterization of these samples will be published elsewhere.[29]

Femtosecond PP-DRS

The experimental setup is summarized here. A train of *ca.* 100-fs pulses with 1 mJ energy at a repetition rate of 1 kHz was generated by a regenerative amplifier system (Quantronix, 4812RGA/4823S/C), which was synchronously pumped by a mode-locked YLF laser (Quantronix, 527DP-H). Seed pulses of 82 MHz centered at 790 nm were supplied from a mode-locked Ti:Sapphire laser (Spectra-Physics, Tsunami: 3960-L2S) pumped by an argon ion laser (Spectra-Physics, BeamLok: 2580C). The final output was split into two beams with almost comparable intensities in order to pump two identical optical parametric generation (OPG)/optical parametric amplification (OPA) systems (Light Conversion, TOPAS). The 620 nm output beam from one OPG/OPA was frequency-doubled in a BBO crystal and used as a pump beam (0.1 ~ 0.03 mJ $(pulse)^{-1}$), and the 620-nm beam from another OPG/OPA was used as a probe beam (1.5 mJ $(pulse)^{-1}$). The probe beam was split into two beams; a minor part, directly detected by a photodiode (Hamamatsu Photonics, Co. Ltd., S2387-66R), was used as a reference. The pump and a major part of the probe beams were collinearly focused with a focal lens ($f = 10$ cm) and overlapped at the sample. The diffusely reflected probe beam was detected by a photodiode, and the output from the photodiodes was collected by two separate gated integrators (Stanford Research Systems, SR250) and digitized with an 8-bit A/D converter (Stanford Research Systems, SR245). Reflectance data were accumulated and recorded by a personal computer as absorption, $1\text{-}R/R_0$, where R and R_0 represent the intensity at a given delay and in the absence of pump pulse, respectively. Both R and R_0 were corrected by the reference beam intensity of each probe pulse and only the absorption for the probe pulse with intensity within a given, typically $\pm 5\%$, fluctuation. The delay between the pump and probe pulses was controlled by an optical delay line including a computer-controlled translation stage with 1 μm (=3.3 fs) resolution and 1 ns maximum delay (Sigma Koki, AS NET-3/STM-160). Before each measurement, the zero point of delay, *i.e.*, the timing of the coincidence of pump and probe beams and spatial overlapping of two beams, was adjusted by measuring the transient absorption of 1,1′-binaphthyl (Tokyo Kasei Kogyo) dissolved in methanol. All the measurements were carried out in air at ambient temperature.

Photoirradiation and product analysis

The photocatalyst (50 mg) was suspended in an aqueous solution (5 cm^3) containing (a) methanol (50 vol.%), (b) Lys (100 μmol), or (c) acetic acid (5 vol.%), and the suspensions were photoirradiated in Ar (a) and (b) or air (c) with magnetic stirring (1000 rpm). In reaction (a), the catalyst was platinized *in situ* by adding $H_2PtCl_6 \cdot 6H_2O$ (Wako Pure Chemical), the amount of which corresponded to 2 wt.% loading of Pt. The platinized TiO_2 powders were recovered and used in reaction (b). Decomposition of acetic acid (reaction (c)) was also examined in air with platinized M-TiO_2 recovered from reaction (a) (c1) or in Ar with unplatinized photocatalysts (c2). Irradiation with light of wavelength $\lambda > 300$ nm from a high-pressure mercury arc (Eiko-sha, 400 W) was performed through a cylindrical Pyrex glass filter and a glass reaction tube (18 mm in diameter and 180 mm in length), so that light at $\lambda > 300$ nm reached the suspension. The temperatures of suspensions under photoirradiation were kept at 298 ± 0.5 K in a thermostatted water bath. Gaseous products, such as H_2 and CO_2, were analyzed by gas chromatography (GC) and products in the liquid-phase were analysed by high-performance liquid chromatography (HPLC). Details of procedures for the photocatalytic reactions investigated and product analyses have been described previously (for methanol,[30] Lys,[31–33] and acetic acid[34,35]).

Results and discussion

PP measurements of bare and metal-loaded TiO_2 powders

Fig. 1 shows representative time-profiles of the transient absorption of bare and Fe-loaded (5%) TiO_2 powders in PP-DRS. As a common feature, a very rapid rise of absorption at 620 nm, within or comparable to the limit of time resolution of *ca.* 500 fs, followed by decay over several hundreds ps, was observed. The rapid rise is thought to be due to capture of photoexcited electrons at a trapping site and broad-band absorption of the trapped electrons in the visible and near-IR regions. Following the pioneering work with PP-DRS of TiO_2 powders and suspensions by Colombo and Bowman,[23] most of the reported PP-DRS data have been analyzed with absorption ($1\text{-}R/R_0$), and the decay profiles could be best fitted to a function of the sum of a second-order rate expression with a constant k_r and very slow decay component, as follows:[24]

$$(\text{absorption}) = \alpha([e]_0/(1 + k_r[e]_0 t) + \text{BL}), \qquad (1)$$

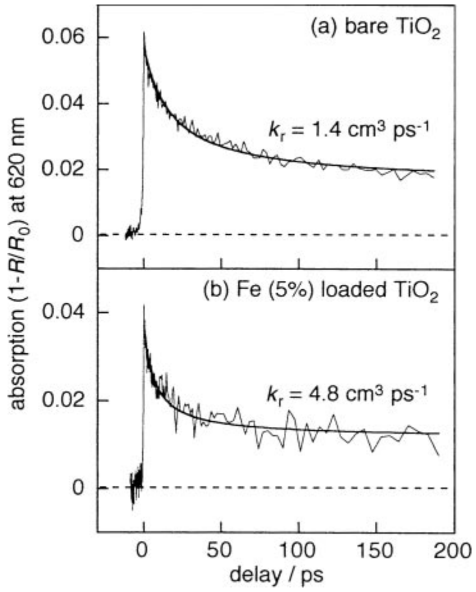

Fig. 1 Representative decay profile of M-TiO_2 powder induced by ultrafast pump (ca. 100 fs). Results of bare and Fe (5%)-loaded TiO_2 powders are shown. Solid line indicates the fitting with eqn. (1).

where $[e]_0$, k_r, t, and BL represent, respectively, the initial concentration of a part of the trapped electrons giving a relatively fast decay just after the pump pulse, the second-order rate constant (cm^3 ps^{-1}), the time delay of the probe pulse (ps), and a component of the long-lived baseline. The parameter α (cm^3) is related to the photoabsorption cross section of the components and the depth of penetration of the pump pulse. This rate equation can be rationalized with the assumption that some of the trapped electrons recombine with positive holes and that the others remain unreacted (BL) in this time region. It is clear by comparing the two profiles in Fig. 1 that the Fe loading gave rise to faster initial decay in the time region of <100 ps, which corresponds to larger k_r. Table 1 summarizes the k_r values of bare and M-TiO_2 samples determined by using eqn. (1), assuming $\alpha = 1$ for every sample. In contrast to first-order decay kinetics, evaluation of the second-order rate constant requires the absolute value of the reaction rate and thereby k_r depends on α. The actual value of α need not be unity and must vary with the measurement conditions. Therefore, the determined value of k_r was a relative measure. Some deeply colored samples containing, for example, 5 mol% of V, Cr, Co, Cu, or Mo absorbed a large part of the probe pulse, leading to much reduced diffuse reflection, and did not allow us to evaluate k_r with high accuracy and reproducibility. It is clear from Table 1 that k_r increased with metal loading for each loaded metal, the loading enhanced the recombination of electrons and holes.

Table 1 Second-order rate constant (k_r)[a] of bare and transition-metal-loaded TiO_2 powders

Loaded metal	k_r/cm^3 ps^{-1}				
	0%	0.3%	1%	2%	5%
Bare[b]	1.4				
V		1.9	3.1	3.7	—
Cr		2.8	2.3	3.4	—
Fe		2.6	4.1	4.6	4.8
Co		2.3	2.5	3.0	—
Cu		2.2	2.3	2.5	—
Mo		1.8	2.1	5.2	—
W		2.3	1.9	2.3	2.2

[a] Estimated from the decay profile of PP-DRS measurement on the assumption that the relatively faster component obeys second-order rate equation. [b] A TiO_2 powder without transition metal.

Effect of transition-metal loading on photocatalytic activity

Fig. 2 shows the rates of formation of (a) H_2, (b) PCA, and (c) CO_2 as functions of the amount of transition-metal loading. Previous reports ((a),[30] (b),[31–33] and (c)[34,35]) indicated that the stoichiometry of the main reactions occurring in our system is

$$CH_3OH = HCHO + H_2 \qquad (2)$$

$$H_2NCH_2(CH_2)_3CH(COOH)NH_2$$
$$= \underline{HN(CH_2)_4CH}COOH + NH_3 \qquad (3)$$

$$CH_3COOH + 2O_2 = 2CO_2 + 2H_2O. \qquad (4)$$

Consequently, we could estimate the overall rate of the redox reactions from the rate of main-product formation. The rate of formation of gas phase products, H_2 and CO_2, was determined from the slope of the plots relative to the amount of products *vs.* irradiation time by considering the initial 1.5 h of irradiation; the rate of PCA formation was determined, by considering only 1.0 h of irradiation. For each reaction, loading of any kind of transition metal gave rise to a decrease in photocatalytic activity and the effect was more significant as the amount of loaded metal increased. Since the high-pressure mercury arc used in this study emits light in the visible region, in addition to UV light, which excites electrons

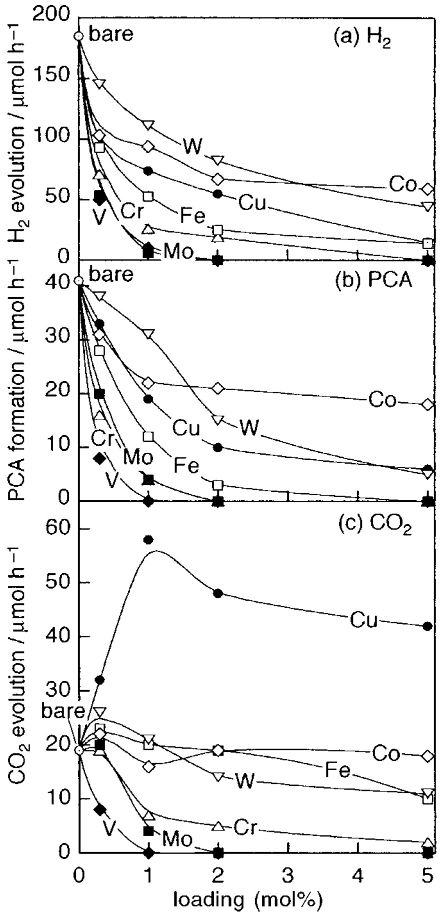

Fig. 2 Rates of main product formation on bare and transition metal-loaded TiO_2 powders *vs.* amount of loaded metal. Platinized M-TiO_2 powders, prepared by *in situ* photodeposition from aqueous H_2PtCl_6, were used in reactions (a) and (b). Bare TiO_2 (○); V-TiO_2 (◆); Cr-TiO_2 (△); Fe-TiO_2 (□); Co-TiO_2 (◇); Cu-TiO_2 (●); Mo-TiO_2 (■); W-TiO_2 (▽).

beyond the band gap, it was expected that loading would be beneficial to the photoactivity. Indeed, absorption of visible light can occur in the presence of a loaded metal. However, the results shown in Fig. 2 clearly indicate that visible light-induced activity had little or no effect and that there was an appreciable reduction in activity by band-gap excitation. Therefore, we can assume that the photoactivity shown in Fig. 2 is essentially due to band-gap excitation.

An exception to the metal-loading effect was Cu in reaction (c); the rate of CO_2 evolution increased with Cu-loading up to 1%, but higher loading gave rise to slightly slower rates compared with the observed maximum value. Possible explanations are: (1) Loaded Cu itself induces photochemical reaction for the decomposition of acetic acid to CO_2. (2) Loaded Cu was dissolved as cations in the aqueous phase (It has been reported that the oxidation of several organic substrates can be considerably accelerated by addition of Cu^{2+} to an aqueous suspension.[36–39]) (3) Loaded Cu is reduced into a metallic state (Cu^0) to act as a co-catalyst, enhancing the photocatalytic activity. The first hypothesis seems unlikely because photoirradiation of a Cu (1%)–SiO_2 (OX50, Nippon Aerosil, 50 m^2 g^{-1}) sample, prepared by a procedure similar to that used for the Cu-TiO_2 samples, resulted in no evolution of CO_2. The second possibility, *i.e.*, acceleration by dissolved Cu species (presumably Cu^{2+}) is even less probable. In the literature, indeed, it has been reported that the presence of dissolved Cu^{2+} ions is beneficial because they can act as electron traps, improving the availability of the holes for production of active hydroxyl radicals;[36,37] if so, the rate for reactions (a) and (b) would be increased, as for reaction (c). On the basis of these considerations, the hypothesis of the presence of deposited metallic Cu could justify the enhancement of the reaction rate. The redox potential of Cu^{2+}/Cu (+0.1 V *vs.* SCE) is more positive than the conduction-band edge of TiO_2. In fact, an ivory-colored suspension of Cu-TiO_2 in aqueous acetic acid solution turned black during the photoirradiation. The deposit may act as a co-catalyst for CO_2 evolution in reaction (c). Similar deposition might occur in reactions (a) and (b), but we noticed only a negligible change in color, due to the presence of pre-deposited Pt. Pt acts as a co-catalyst and consequently might obscure the effect of Cu. The photocatalytic activity for H_2 and PCA production of the unplatinized Cu-TiO_2 sample was appreciable but smaller than that of the corresponding platinized sample.

Dependence of photocatalytic activity on k_r

Fig. 3 shows the correlations of the rates of reaction (a) (upper) and (b) (lower) with k_r, determined by PP-DRS and summarized in Table 1. As has been previously reported,[24] there was an almost linear relation between k_r values measured in air and in suspension for several TiO_2 samples. Furthermore, a negligible difference was obtained with and without O_2. Consequently, the k_r value obtained in the powder diffuse reflection system was used to examine the correlation with photocatalytic activity in aqueous suspensions. Although both plots were fairly scattered, it was clear that the rate tended to decrease with increase in k_r. We assumed that the activity for these reactions was inversely proportional to the increase in k_r, *i.e.*, the net activity was dominated by the electron–hole recombination rate. We attempted to measure k_r for the platinized M-TiO_2 samples which were used in reaction (a) or (b) but failed due to the lack of reflection of the probe beam on their highly colored surfaces. However, in separate PP-DR analyses using several commercial and synthesised TiO_2 powders without transition-metal-loading, an almost linear relation between the k_r values of platinized and unplatinized samples was observed.[40] Therefore, the k_r values of unplatinized TiO_2 powders were used for convenience throughout this study.

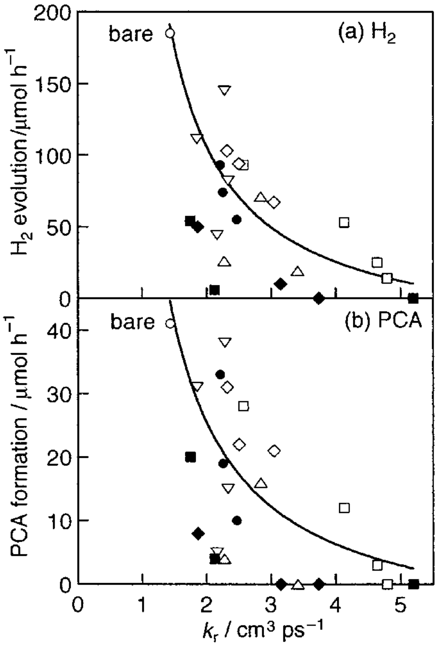

Fig. 3 Relation between k_r values and rate of main product formation. Upper, H_2 evolution (reaction (a)); lower, PCA formation (reaction (b)). The meanings of the symbols same as those in Fig. 2.

The relation between the rate of reaction (c) and k_r (Fig. 4) was rather ambiguous, even if the data obtained using Cu-TiO_2 samples were not considered. The reciprocal relation between k_r and the reaction rate cannot be applied to the results shown in Fig. 4, as the reaction rate in this case appears to be independent of k_r. This tendency appears clearer if the plots of the results of Cr- and V-TiO_2 samples are removed from both figures, as these powders showed much less significant photocatalytic activity in all the reaction systems. Although no experimental evidence has so far been reported, the activity of M-TiO_2 for reaction (c) may be governed by factors other than the recombination rate, such as redox reactions consuming e^- and h^+, and/or metal surface coverage inhibiting e^- (or h^+) transfer to the reacting substrate(s) or the adsorption of the substrate(s). On the basis of these considerations, the difference in k_r dependence, reciprocal or independent, will be discussed and rationalised in the following sections.

Apparently, there were two significant differences in the experimental conditions under which the reactions (a) and (b) and (c) were carried out: (1) the absence and presence of O_2

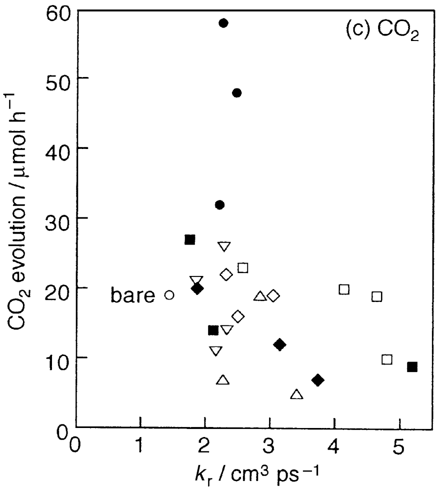

Fig. 4 Relation between k_r values (cm^{-3} ps^{-1}) rate of CO_2 evolution in reaction (c). The meanings of the symbols are as in Fig. 2.

and (2) the presence and absence of Pt deposits for (a) and (b) and (c), respectively. In order to examine the influences of these factors, the following two additional experiments were performed: decomposition of acetic acid under air with platinized M-TiO_2 powders (c1) and under an Ar atmosphere with unplatinized M-TiO_2 (c2). In these experiments, M-TiO_2 samples showing photoactivity similar to that of bare TiO_2 in reaction (c) were used to evaluate the dependence of photocatalytic activity on k_r as a sole parameter. Fig. 5–7 show the results. For reaction (c1), the rate increased *ca.* three-fold for bare TiO_2, but the ratio between reaction rates observed with platinized and unplatinized samples *vs.* the k_rs decreased to 1 when k_r was >4 (Fig. 5). Thus, a k_r dependence of the (c1) reaction similar to those of reactions (a) and (b) was obtained.

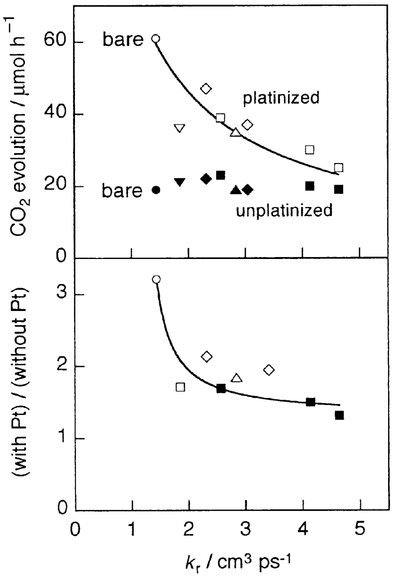

Fig. 5 Rate of CO_2 evolution *vs.* k_r values. Upper, platinized (open symbols) and unplatinized (filled symbols) M-TiO_2 in the presence of O_2; lower, ratio of these rates, (platinized/unplatinized). Pt was deposited by photoplatinization in reaction (a). Circles, triangles, squares, diamonds, and inverted triangles denote bare TiO_2, Cr-TiO_2, Fe-TiO_2, Co-TiO_2, and W-TiO_2 samples, respectively.

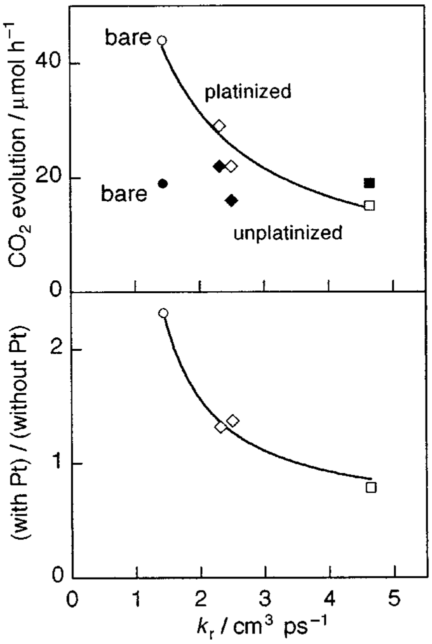

Fig. 6 Rate of CO_2 evolution *vs.* k_r values. Upper, platinized and unplatinized M-TiO_2 in the presence of O_2; lower, ratio of these rates, (platinized/unplatinized). Pt was deposited from colloidal Pt. The meanings of the symbols are as in Fig. 5.

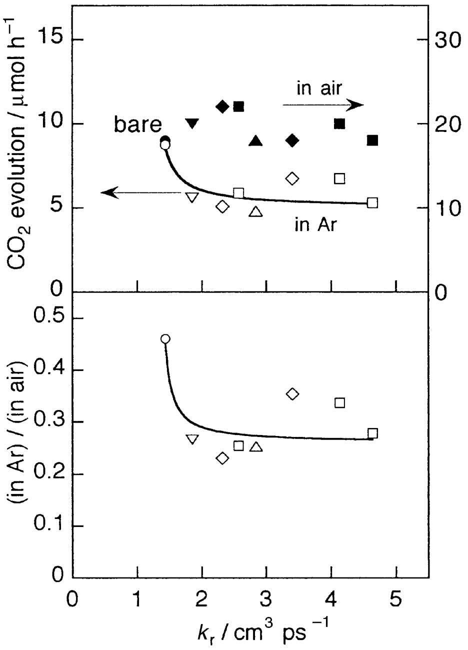

Fig. 7 Rate of CO_2 evolution as a function of k_r values. Upper, results in Ar (open symbols) and in air (closed symbols) for the unplatinized samples; lower, ratio of these rates (Ar/air). The meanings of the symbols are as those in Fig. 5.

It is known that the photocatalytic activity on platinized TiO_2 depends strongly on the procedure of Pt deposition, *e.g.*, the difference in photocatalytic activity could be explained in terms of the distribution of Pt deposited on the TiO_2 particles, not on the total amount of Pt deposit.[41] Depending on the intrinsic photocatalytic activity of M-TiO_2, the *in situ* photoplatinization method used in this study might lead to a different Pt distribution. Although the difference, if it actually exists, may be a measure of the intrinsic photocatalytic activity, this possibility could be excluded by performing the following experiment. The photocatalytic reaction (c1) was carried out by using platinized M-TiO_2 prepared by deposition from colloidal Pt. Since the platinization was achieved without any chemical reaction, similar distributions of Pt particles could be expected.[32,42,43] Fig. 6 shows the results. A similar relation between activity and k_r was also observed in this case, indicating that the influence of different Pt distributions among the M-TiO_2 powders could be neglected, *i.e.*, the observed k_r dependence of the photocatalytic activity is caused by the influence of the loaded transition-metal. In other words, the platinization made the k_r dependence noticeable.

In reaction (c2), the photocatalytic activity also became k_r-dependent (Fig. 7). The activity decreased to *ca.* 2/3 of that of bare TiO_2 due to the transition-metal loading, though the activity of the bare TiO_2 was almost half of that under air. The stoichiometry of this photocatalytic reaction was not clear, although it is clear that acetic acid was decomposed to liberate CO_2, and that the rate was much slower than in the other systems. However, it should be noted that the presence of O_2 enhances the photocatalytic reaction and, at the same time, obscures the influence of e^-–h^+ recombination, as was evaluated with k_r. Thus, the k_r dependence disappears in the presence of O_2, while it is intensified by platinization.

A model of the reaction kinetics

As described above, we observed that transition-metal loading accelerates the e^-–h^+ recombination, resulting in the reduction of photocatalytic activity of, in particular, the platinized M-TiO_2, while the activity of the unplatinized M-TiO_2 in the presence of O_2 seems to be almost independent of the loading. Since (1) photocatalytic reactions proceed *via* photoexcitation of electrons beyond the band gap to yield e^- and h^+ and (2) these redox active species react with surface-adsorbed substrates (or otherwise recombine leading to no chemical reaction), the rate of recombination must be included in the rate expression. The following discussion on the model of the reaction kinetics is based on the assumptions that only the band-gap excitation of TiO_2 participates, even though M-TiO_2 had an extended absorption, and also that the rate of e^-–h^+ formation in each M-TiO_2 photocatalyst is the same. When first-order rates are assumed for convenience for both recombination of e^-–h^+ (mutual recombination) and surface reaction of e^- and h^+ with the substrates, the rate of e^-–h^+ escaping from their recombination (r_{esc}) is given, using a steady-state approximation for e^-–h^+ pairs, as follows:

$$r_{esc} = I\phi kC/(kC + k_r), \quad (5)$$

where I and ϕ are the light flux of excitation and the probability of light absorption to produce e^- and h^+. A rate constant (k) and surface concentration of substrate (C) were also defined tentatively. In this "homogeneous" model, an e^-–h^+ pair behaves as a photoexcited molecule in a solution containing a reaction substrate of concentration C. When k_r is comparable to or larger than kC, r_{esc} should be inversely proportional to k_r, as observed in reactions (a) and (b). Thus, it is expected that e^-–h^+ recombination is detrimental to the photocatalytic activity unless the pairs react with the surface-adsorbed substrate(s). On the other hand, if kC is much larger than k_r, *i.e.*, the surface reaction(s) proceeds efficiently before the mutual recombination, r_{esc} becomes independent of k_r, as was observed for reaction (c). It seems reasonable to expect that the surface-adsorbed O_2 reacts with e^-. By assuming that the overall photocatalytic reaction rate ($r_{overall}$) is proportional to r_{esc} and that r_{esc} is governed by eqn. (5), $r_{overall}$ for reaction (c) must be larger than that for reaction (a) or (b). If k_r is negligible, r_{esc} is equal to $I\phi$ *i.e.*, the quantum efficiency is 100%. However, almost comparable rates, corresponding at most to only a few% of quantum efficiency, were determined, indicating that other factors might be responsible for the decrease in $r_{overall}$. For example, the reverse reaction of intermediate species formed *via* the surface reaction may cause the reduction in $r_{overall}$.

Another explanation for the different k_r dependences is based on the assumption that the distance between the place where e^-–h^+ pairs form and react with the substrate(s) depends on the type of photocatalytic reaction and on the experimental conditions used. It has been reported that platinization of TiO_2 efficiently enhances activity for photocatalytic dehydrogenation of propan-2-ol and deaminocyclization of Lys (reaction (b)).[41] For these reactions, it was proved that TiO_2 particles loaded with at least one Pt deposit show sufficient ability for propan-2-ol dehydrogenation and that further Pt loading has a negligible or, rather, a negative effect. This indicates that e^- formed in a relatively small (20–50 nm; corresponding to *ca.* 50 m^2 g^{-1}) TiO_2 particle can migrate within the whole volume of the particle. Since reaction (b) proceeds *via* a redox combined mechanism including oxidation and reduction by h^+ and e^-, respectively, a larger number of Pt deposits is needed to decrease the distance between the site for oxidation of Lys and for reduction of the reaction intermediate. Thus, redox reactions occur at separate sites also in the reactions (a) and (b). On the other hand, reaction (c) does not need Pt loading. It has been presumed that oxidation of surface-adsorbed acetic acid by h^+ and reduction of O_2 by e^- occur at neighbouring sites. On the basis of these considerations, it seems reasonable to assume that the rates of reactions (a) and (b) depend on k_r since e^- (or h^+) must migrate in the bulk or on the surface of a TiO_2 particle unless they recombine at the recombination centres. The rate of reaction (c), on the other hand, is almost independent of k_r because there is no, or only negligible, migration of e^- (or h^+) essential for the occurrence of photocatalytic reactions.

Summary and conclusion

Several studies have suggested acceleration of e^-–h^+ recombination by transition metal doping and/or loading of TiO_2,[9–14] but there is insufficient experimental evidence because the recombination dynamics is much faster than the detection limit of conventional time-resolving measurements. The present study on PP-DR spectroscopy of transition metal-loaded TiO_2 powders directly revealed acceleration of e^-–h^+ recombination by metal loading. Furthermore, two different relations between photocatalytic activity and recombination rate were found, depending on the photocatalytic system studied and on the experimental conditions. Reduction of photocatalytic activity by metal loading for dehydrogenation of methanol and conversion of Lys into PCA (typical photo-reactions carried out in deaerated conditions and in the presence of Pt deposits on the surface of the catalyst) indicated some difficulty in improving the photocatalytic activity, *e.g.*, an extension of the response in the visible-light region by loading other metals or metal oxides on semiconducting materials. In contrast, the results of photocatalytic oxidation of acetic acid suggested that it might be possible to induce a visible light response by metal loading for photocatalytic oxidation systems in aerated conditions, such as decomposition and/or mineralisation of organic compounds, without reducing the primary photocatalytic activity in the UV region. Thus, we have shown the effect of transition-metal loading of TiO_2 powders on photocatalytic activity and correlated the relation between photocatalytic activity and recombination rate. These results should be useful for the design of further functionalized photocatalytic materials for different kinds of reactions.

Acknowledgements

The present work was partly supported by a Grant-in-Aid for Scientific Research in Priority Area of "Electrochemistry of Ordered Interfaces" (No. 11118208) from the Ministry of Education, Science, Sports, and Culture, Japan.

References

1 A. Mills and P. Sawunyama, *J. Photochem. Photobiol. A*, 1997, **108**, 1.
2 K. Sayama and H. Arakawa, *J. Chem. Soc., Chem. Commun.*, 1992, 150.
3 S. Tabata, H. Nishida, Y. Masaki and K. Tabata, *Catal. Lett.*, 1995, **34**.
4 M. Anpo and H. Yamashita, in *Heteroreneous Photcatalysis*, ed. M. Schiavello, Wiley, New York, 1997, p. 531.
5 M. A. Fox and M. T. Dulay, *Chem. Rev.*, 1993, **93**, 341.
6 B. Ohtani, in *Trends in Photochemistry and Photobiology*, ed. Council of Scientific Information, Research Trends, Trivandrum (India), 1994, p. 531.
7 M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chem. Rev.*, 1995, **95**, 69.
8 A. L. Linsebigler, G. Lu and J. T. Yates, *Chem. Rev.*, 1995, **95**, 735.
9 E. Borgarello, J. Kiwi, M. Grätzel, E. Pelizzetti and M. Visca, *J. Am. Chem. Soc.*, 1982, **104**, 2996.
10 Z. Luo and Q. H. Gao, *J. Photochem. Photobiol. A*, 1992, **63**, 367.
11 K. E. Karakitsou and X. E. Verykios, *J. Phys. Chem.*, 1993, **97**, 1184.
12 N. Serpone and D. Lawless, *Langmuir*, 1994, **10**, 643.
13 T. Ohno, F. Tanigawa, K. Fujihara, S. Izumi and M. Matsumura, *J. Photochem. Photobiol. A*, 1999, **127**, 107.
14 M. Anpo, Y. Ichihashi, M. Takeuchi and H. Yamashita, *Res. Chem. Intermed.*, 1998, **24**, 143.
15 J. Z. Zhang, R. H. O'Neil and T. W. Roberti, *Appl. Phys. Lett.*, 1994, **64**, 1989.
16 J. Z. Zhang, R. H. O'Neil, T. W. Roberti, J. L. McGowen and J. E. Evans, *Chem. Phys. Lett.*, 1994, **218**, 479.

17 J. Z. Zhang, R. H. O'Neil and T. W. Roberti, *J. Phys. Chem.*, 1994, **98**, 3859.

18 J. J. Cavaleri, D. E. Skinner, J. D. P. Colombo and R. M. Bowman, *J. Chem. Phys.*, 1995, **103**, 5378.

19 J. J. Cavaleri, D. P. Colombo, Jr. and R. M. Bowman, *J. Phys. Chem. B*, 1998, **102**, 1341.

20 D. E. Skinner, J. D. P. Colombo, J. J. Cavaleri and R. M. Bowman, *J. Phys. Chem.*, 1995, **99**, 7853.

21 D. P. Colombo, Jr. and R. M. Bowman, *J. Phys. Chem.*, 1995, **99**, 11752.

22 D. P. Colombo, Jr., K. A. Roussel, J. Saeh, D. E. Skinner, J. J. Cavaleri and R. M. Bowman, *Chem. Phys. Lett.*, 1995, **232**, 207.

23 D. P. Colombo, Jr. and R. M. Bowman, *J. Phys. Chem.*, 1996, **100**, 18445.

24 B. Ohtani, H. Kominami, R. M. Bowman, P. Colombo, Jr., H. Noguchi and K. Uosaki, *Chem. Lett.*, 1998, 579.

25 A. Furube, T. Asahi, H. Masuhara, H. Yamashita and M. Anpo, *Chem. Lett.*, 1997, 735.

26 A. Furube, T. Asahi, H. Masuhara, H. Yamashita and M. Anpo, *J. Phys. Chem. B*, 1999, **103**, 3120.

27 G. Rothenberger, J. Moser, M. Gräzel, N. Serpone and D. K. Sharma, *J. Am. Chem. Soc.*, 1985, **107**, 8054.

28 N. Serpone, D. Lawless and R. Khairutdinov, *J. Phys. Chem.*, 1995, **99**, 16655.

29 A. D. Paola, S. Ikeda, G. Marcí, B. Ohtani, L. Palmisano and M. Schiavello, to be published.

30 S.-i. Nishimoto, B. Ohtani and T. Kagiya, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 2467.

31 B. Ohtani, S. Tsuru, S.-i. Nishimoto, T. Kagiya and K. Izawa, *J. Org. Chem.*, 1990, **55**, 5551.

32 B. Ohtani, J.-i. Kawaguchi, M. Kozawa, S.-i. Nishimoto, T. Inui and K. Izawa, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 1103.

33 B. Ohtani, J.-i. Kawaguchi, M. Kozawa, Y. Nakaoka, Y. Nosaka and S.-i. Nishimoto, *J. Photochem. Photobiol. A*, 1995, **90**, 75.

34 H. Kominami, J.-i. Kato, Y. Takada, Y. Doushi, B. Ohtani, S.-i. Nishimoto, M. Inoue, T. Inui and Y. Kera, *Catal. Lett.*, 1997, **46**, 235.

35 H. Kominami, J.-i. Kato, M. Kohno, Y. Kera and B. Ohtani, *Chem. Lett.*, 1996, 1051.

36 A. Fujihira, Y. Satoh and T. Osa, *Chem. Lett.*, 1981, 1053.

37 A. Sclafani, L. Palmisano and M. Schiavello, *Res. Chem. Intermed.*, 1992, **18**, 211.

38 M. Bideau, B. Claudel, L. Faure and H. Kazouan, *J. Photochem. Photobiol. A*, 1991, **61**, 269.

39 M. I. Litter, *Appl. Catal. B*, 1999, **23**, 89.

40 S. Ikeda, H. Kominami, Y. Kera, H. Noguchi, K. Uosaki and B. Ohtani, *J. Phys. Chem.*, to be submitted.

41 B. Ohtani, K. Iwai, S.-i. Nishimoto and S. Sato, *J. Phys. Chem. B*, 1997, **101**, 3349.

42 A. Mills, *J. Chem. Soc., Chem. Commun.*, 1982, 367.

43 P.-A. Brugger, P. Cuendet and M. Gräzel, *J. Am. Chem. Soc.*, 1981, **103**, 2923.