Photocatalytic Reaction Kinetics on TiO₂ Thin Films under Light-Limited and Mass Transport-Limited Conditions

By Y. Ohko¹, K. Ikeda¹, T. N. Rao¹, K. Hashimoto^{2.*} and A. Fujishima¹

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This paper describes our recent studies on kinetics and mechanism of photocatalytic decomposition of reactions on TiO_2 thin films under weak UV illumination. Separate observation of reactions at oxidation and reduction sites of a photocatalyst indicated that the radical chain reactions occur at oxidation of 2-propanol and acetaldehyde were determined by the normalized absorbed photon number (I_{norm}). High QY values were obtained for acetaldehyde in comparison to 2-propanol indicating the existence of radical chain reactions for the former reaction. Based on the kinetic studies of gas phase 2-propanol degradation under wide range of light intensities and initial concentrations, we have mapped various regions on a light intensity vs. initial reactant concentration plot, showing pure mass transport-limited conditions and pure light intensity-limited conditions.

Introduction

The use of TiO_2 as a photocatalyst for environmental cleanup is of great interest because of its high oxidation power and chemical inertness. The photogenerated holes in TiO_2 have strong oxidizing power (~3.0 V vs. SHE), enabling it to oxidize nearly all types of toxic organic compounds. Extensive studies have been carried out for the purpose of air and water purification [1-4]. Earlier, high intensity light sources were mainly used in most photocatalytic research to achieve high degradation rates [5, 6]. The use of weak UV light sources such as sunlight and black-light-type fluo-

^{&#}x27; The University of Tokyo, Department of Applied Chemistry,

Graduate School of Engineering, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

² The University of Tokyo, Research Center for Advanced Science and Technology,

⁴⁻⁶⁻¹ Komaba, Meguro-ku, Tokyo 153-8904, Japan

^{*} Corresponding author.

rescent lamps has gained much importance [7-9] after the demonstration of photodegradation of oil and chemical slicks on water with TiO₂-coated glass microbubbles by Heller's group [10]. The role of oxygen in photocatalysis is highly significant as it prevents carrier recombination by trapping the photogenerated electrons [11] and participates in the radical chain reactions which in turn participate in the photodegradation reactions [12]. The high mass-transport rates for oxygen in the gas-phase results in efficient degradation of gas-phase organic compounds.

Our main interest in the field of photocatalysis is to make use of the weak UV light available in the solar radiation and in ordinary fluorescent lamps to decompose toxic gas-phase organic contaminants, so that the application of photocatalysis in indoor living and working environments becomes more practical. For example, a typical UV light intensity level of $1 \,\mu$ W/cm² is obtained on the floors of rooms illuminated with white fluorescent lamps. The transport of the reactants in living environment takes place by natural convection. We have demonstrated the self-cleaning, antibacterial and deodorizing effects under low intensity UV illumination using TiO₂-containing materials such as paper [13], tiles [14] and glass [15, 16]. Such materials were found to exhibit high photocatalytic activity for the degradation of acetaldehyde, an odor-causing gas in indoor air, particularly in cigarette smoke [17, 18]. Generally, odors that are objectionable to humans are due to compounds which are present only in the order of 10 parts per million by volume (ppmv). Hence, the UV light available from ordinary fluorescent lighting should be sufficient to decompose such compounds in the presence of TiO_2 . It is also interesting to study the kinetics of photocatalytic reactions under low-intensity UV illumination in order to obtain new insight about TiO₂ photocatalysis.

In this paper, we summarize our recent work on the mechanistic and kinetic studies on photocatalytic decomposition of alcohols in TiO₂-thin films under low-intensity UV illumination. To understand the mechanism of ethanol degradation which involves radical chain reaction, we have used microelectrode technique which enable the separate monitoring of reactions at oxidation and reduction sites of photocatalyst in aqueous solutions containing dissolved oxygen [19]. For kinetic studies, we have chosen 2-propanol as a substrate because it undergoes efficient photodegradation to produce acetone, which undergoes further reactions at a much slower rate [20]. The quantum yield values obtained for this reaction were compared with the values obtained for the photodegradation of acetaldehyde which involves radical chain reactions [21]. Due to the existence of radical chain reactions, the QY for photodegradation of acetaldehyde was expected to be very high in comparison to the values for 2-propanol. Finally, on the basis of results obtained with 2-propanol, we have mapped various regions on a light intensity vs. initial reactant concentration plot, showing pure mass transport conditions and pure light intensity-limited conditions [22].

Experimental section

The mechanism of the photodecomposition of ethanol was investigated by using microelectrode technique. The details of the microelectrode fabrication were reported elsewhere [19]. Briefly, a carbon fiber was inserted into a thin Pyrex glass tube, and, the tube was pulled by heating to obtain a glass-coated fiber. After cutting the glass-coated fiber it was polished to generate a carbon disk. For electrochemical studies, these microelectrodes were placed above a partially Pd-covered TiO₂ films which act as a model for metal modified TiO₂ particle. The concentrations of dissolved O₂ and H₂O₂ were determined amperometrically by positioning the microelectrode above TiO₂ site or Pd site on the photocatalyst surface under illumination. The measurements were carried out in an aqueous solution containing 0.1 M K_2SO_4 both in the absence and in the presence of ethanol.

For the kinetic analysis of photocatalytic degradation of gas-phase 2propanol and acetaldehyde, we have used TiO₂ films which were prepared by a spin-coating method, using a commercial TiO₂ anatase aqueous sol. The roughness factor of the film was found to be ~150. An O₂ (20%)-N₂ mixture adjusted to a relative humidity of 50% was used to fill the reaction vessel. The gas mixture with 2-propanol was prepared by injecting the measured quantity of 2-propanol-saturated gas (approximately 5 vol% in the dry O₂-N₂ gas mixture) into the reaction vessel. In case of acetaldehyde, commercial gas (5 vol% in N₂) was used for injection. The TiO₂ thin film was illuminated with a Hg-Xe lamp. Neutral density filters were used to control the intensity. The ratio of the photon flux absorbed by the TiO₂ film to the incident photon flux was determined to be ~0.65 [20]. The details about materials and methods used in this work were described previously [20-22].

Results and discussion

In order to understand the mechanism of photocatalysis involving radical chain reactions we have studied the photodecomposition of ethanol in aqueous solution using microelectrode technique [19]. It can be expected that the dissolved oxygen in the solution gets consumed at the reduction site and production of oxygen takes place at the oxidation site due to water oxidation. The oxygen reduction current at both Pd (reduction) and TiO₂ (oxidation) sites were measured amperometrically in the absence of ethanol. The cathodic current (due to oxygen reduction) at the microelectrode decreased above Pd and increased above TiO₂ under illumination.

$$\mathrm{TiO}_2 + \mathrm{h}\,v \to \mathrm{h}^+ + \mathrm{e}^- \tag{1}$$

$$2 \operatorname{H}_{2}O + 4 \operatorname{h}^{+} \rightarrow O_{2} + 4 \operatorname{H}^{+} (\text{above Ti}O_{2})$$
⁽²⁾



Fig. 1. Separate detection of concentration changes of dissolved O_2 (proportional to cathodic current, -1000 mV vs. SCE, A) or H_2O_2 (proportional to anodic current, +1000 mV vs. SCE, B) at TiO₂ (oxidation) and Pd (reduction) sites which results from the photocatalytic reaction in the presence of ethanol.

$$O_2 + e \rightarrow O_2 \text{ (above Pd)}$$
 (3)

$$O_2 + H^+ \to HO_2^{\cdot} \tag{4}$$

In the presence of ethanol (5 vol%), however, the cathodic current at the microelectrode decreased above both Pd and TiO₂ sites, the decrease being more above TiO₂ site than that above Pd site (Fig. 1a). These results



Fig. 2. Quantum yield dependence on absorbed photons at various initial 2-propanol concentrations.

indicate that the oxygen was consumed even at TiO_2 (oxidation) sites due to the participation of molecular oxygen in the photooxidation reactions at oxidation sites. The oxidation of ethanol is initiated by the following reactions:

$$h^+ + H_2 O \rightarrow OH + H^+$$
 (5)

$$OH + CH_3CH_2OH \rightarrow CH_3C'HOH + H_2O.$$
(6)

The ethanol radicals can react with molecular oxygen resulting in the formation of final products, acetaldehyde and H_2O_2 at TiO₂ sites. Fig. 1b shows the anodic current at the microelectrode due to oxidation of H_2O_2 above Pd and TiO₂ sites. The appearance of anodic current at TiO₂ site confirms the formation of H_2O_2 as expected. The termination of radical chain reaction occurs by a peroxyl radical coupling reaction, producing molecular oxygen [19].

Unlike in the case of ethanol, the photocatalytic decomposition of 2propanol does not involve chain reactions. Hence, it acts as a simple model substrate for kinetic studies. Furthermore, it is efficiently photodecomposed to acetone, which can be detected by gas chromatography with high sensitivity. The mechanism of photodecomposition of 2-propanol does not involve chain reactions [20]. Only one photon participates in the generation of one molecule of acetone. Hence the apparent quantum yield is equal to the ratio of the number of generated acetone molecules to number of absorbed photons.



Fig. 3. Quantum yield dependence on the normalized absorbed photon number (I_{norm}) at various initial 2-propanol concentrations.

Fig. 2 shows the semilog plots of absorbed photons (I) versus apparent QY values for acetone generation. These plots were obtained for various initial concentrations. The QY values in each plot increased gradually with decreasing I and finally saturated except for the lowest initial concentration (1 ppmv). Thus, light-limited condition was reached at lower light intensities. The maximum concentration observed was $\sim 28\%$ for the highest 2-propanol concentration (1000 ppmv). Another observation in this figure is that when the 2-propanol concentration was decreased, the curve shifted to the lower light intensity direction. The shift was not systematic with the concentration. This indicates that the QY value is not determined by the ratio of the light intensity to the gas concentration.

Fig. 3 shows the variation of QY as a function of normalized photon number (I_{norm}). This number is defined as the ratio of number of absorbed photons (per second) to the number of adsorbed 2-propanol molecules. The plots obtained for different initial concentrations of 2-propanol fall on the same curve. The value of QY increase as I_{norm} decreased and finally became constant at ~28% for I_{norm} values below 10⁻⁴/s. These results indicate that either 'OH or 2-propanol molecules diffuse on the TiO₂ surface and the collision probability of these species determine the efficiency of the decomposition reaction. From the Fig. 3, one can expect a QY value of 28% even for the lowest initial concentration, 1 ppmv at lower values of I_{norm} . Based on this concentration, we have calculated intermolecular distance of



Fig. 4. Comparison of quantum yield dependence on I_{norm} between 2-propanol and acetaldehyde.

adsorbed 2-propanol of ca. 11 from adsorption isotherm [20]. Hence the possible diffusion length of either 'OH radicals or 2-propanol can be at least 11 nm.

For comparison, we have also plotted the QY values for acetaldehyde degradation, as a function of I_{norm} (Fig. 4) together with the plot corresponding to 2-propanol (1000 ppmv). The calculation of QY for this reaction was described earlier [21]. Interestingly, the curves for both acetaldehyde and 2-propanol coincided over a wide range of I_{norm} values. This observation indicates that the 'OH radicals are highly reactive with many kinds of organic molecules irrespective of their nature. The high QY values (>100%) for the acetaldehyde degradation is due to the involvement of the radical chain reactions.

The degradation of aldehydes in the presence of O_2 is known to proceed via radical chain reactions on the TiO₂ surface. Either the photogenerated hole or the 'OH radical reacts with acetaldehyde, abstracting a hydrogen atom to form a CH₃C'O radical which reacts further with O_2 to produce unstable CH₃(CO)OO' radical. This peroxo radical reacts with another acetaldehyde, subsequently generating acetic acid and the CH₃C'O radical. Over all, only 0.5 photons participate in generating one molecule of acetic acid. The CH₃C'O radical is recycled back to react with O_2 . Subsequently, CO₂ is generated from acetic acid at the expense of 1.5 photons. If these radical reactions are involved, QY values are expected to exceed 100%. This is evident from the data shown in Fig. 4.



Fig. 5. Dependence of reaction rate on absorbed photons at various initial 2-propanol concentrations.

We have carried out further studies on photodegradation of 2-propanol at relatively higher intensities in order to achieve mass transport-limited conditions. Fig. 5 shows log-log plots of the 2-propanol degradation rates (R) at different initial concentrations versus the number of photons (I) absorbed by the TiO₂ per unit time. These studies were carried out at relatively higher intensity range of UV illumination in order to obtain mass transportlimited conditions [22]. Although, the degradation rate for each concentration increased with increasing number of absorbed photons at lower light intensities, it gradually saturated and finally reached completely mass transport-limited conditions. The I values at which mass transport-control is attained, increased with increasing initial 2-propanol concentrations. Based on these results, together with the results obtained under extremely lowintensity UV illumination, we have mapped various regions on a light intensity vs. initial reactant concentration plot, showing pure mass transport limited conditions and pure light intensity-limited conditions (Fig. 6). It is interesting to note that the plot covers 6 orders of magnitude of reactant concentration and 8 orders of magnitude of light intensity.

Conclusions

The kinetics and mechanism of degradation of alcohols were investigated. The photocatalytic reactions occurring at oxidation and reduction sites were monitored separately by determining the dissolved oxygen and H_2O_2 using a



Fig. 6. Plots of light intensity vs. initial reactant concentration showing pure mass transport-limited and pure light intensity-limited conditions for photodegradation of gas-phase organics.

microelectrode. These results indicated that the photodegradation of ethanol involves radical chain reactions. The quantum yields for photodegradation of gas-phase 2-propanol and acetaldehyde were obtained by using the values of normalized absorbed photon number (I_{norm}). The high QY values (>100%) obtained for acetaldehyde in comparison to the values (~28%) obtained for 2-propanol were attributed to the involvement of radical chain reactions in the former reaction. Based on the results obtained from the photodegradation of 2-propanol, we have been able to map out a wide range of experimental conditions, covering 6 orders of magnitude of reactant concentration and 8 orders of magnitude of light intensity, in terms of mass transport vs. light intensity control. From the intensity vs. concentration plot, the maximum value of light intensity which is necessary to obtain the maximum reaction rate for a given target concentration of reactant can be estimated.

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