

## PHOTOCATALYTIC KINETICS OF GASEOUS ACETALDEHYDE DEGRADATION ON LOW INTENSITY ULTRA VIOLET IRRADIATED TiO<sub>2</sub>

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### ABSTRACT

**PHOTOCATALYTIC KINETICS OF GASEOUS ACETALDEHYDE DEGRADATION ON LOW INTENSITY ULTRA VIOLET IRRADIATED TiO<sub>2</sub>** The kinetics of photocatalytic degradation of gaseous acetaldehyde with semiconductor catalyst TiO<sub>2</sub> was studied. The experiment was carried out using TiO<sub>2</sub> photocatalyst prepared from titanium tetrachloride (TiCl<sub>4</sub>) and titanium(IV) isopropoxide (Ti(OPr)<sub>3</sub>) as the starting materials. Commercially available highly active TiO<sub>2</sub> from Merck was used for purposes of comparison. The TiO<sub>2</sub> films were prepared on soda lime plates and an SiO<sub>2</sub>-coated soda lime plate using sol-gel method and dip-coating techniques. The photocatalytic kinetics of the catalysts were assessed by measuring the photodegradative oxidation of gaseous acetaldehyde at various initial concentrations, UV intensities, and shapes of catalyst. The Merck powder shown the highest photocatalytic activity. All reactions proceeded with approximately first-order reaction kinetics (as indicated from the linear transforms  $\ln(C_0/C)$  as function of irradiation time), especially for the relatively low initial concentration. Meanwhile, at high initial concentration of acetaldehyde, photocatalytic reactions occurred with approximately zero-order kinetics. TiO<sub>2</sub> film photocatalyst supported on soda lime plate shown lower photocatalytic activity than the powder one, however, when the films were coated on SiO<sub>2</sub>-coated soda lime plate, photocatalytic activity of the resulting film increased and even higher than that of the powder form.

**Key words :** TiO<sub>2</sub>, photocatalytic, UV radiation, kinetic.

### ABSTRAK

**KINETIKA FOTOKATALITIK DEGRADASI GAS ASETALDEHIDA PADA TiO<sub>2</sub> YANG DIRADIASI ULTRA VIOLET BERINTENSITAS RENDAH.** Kinetika degradasi fotokatalitik gas asetaldehida dengan katalis semikonduktor TiO<sub>2</sub> telah diteliti. Percobaan dilakukan menggunakan fotokatalis TiO<sub>2</sub> yang dipreparasi dari bahan awal titanium tetraklorida (TiCl<sub>4</sub>) dan titanium(IV) isopropoksida (Ti(OPr)<sub>3</sub>). TiO<sub>2</sub> komersial yang sangat aktif dari Merck digunakan untuk perbandingan. Film TiO<sub>2</sub> dipreparasi dengan metoda sol-gel dan teknik pelapisan *dip-coating* pada penyangga kaca pelat *soda lime* dengan dan tanpa dilapisi dengan SiO<sub>2</sub>. Kinetika fotokatalitik katalis dikaji melalui pengukuran oksidasi fotokatalitik gas asetaldehida pada berbagai konsentrasi awal, intensitas sinar ultra violet, dan bentuk katalis. Serbuk TiO<sub>2</sub> Merck memperlihatkan aktivitas fotokatalitik tertinggi. Semua reaksi berjalan hampir seluruhnya menurut kinetika orde pertama (seperti diindikasikan dari transformasi linier  $\ln(C_0/C)$  sebagai fungsi waktu iradiasi), terutama untuk konsentrasi awal yang relatif rendah. pada konsentrasi gas asetaldehida yang tinggi, reaksi fotokatalitik berlangsung dengan orde mendekati nol. Katalis film TiO<sub>2</sub> yang tersangga di atas pelat *soda lime* lebih rendah aktivitasnya dari katalis bentuk serbuknya, namun ketika film TiO<sub>2</sub> dilapiskan di atas pelat *soda lime* yang sebelumnya telah dilapisi film SiO<sub>2</sub>, aktivitasnya jauh meningkat dan bahkan lebih baik dari bentuk serbuknya.

**Kata kunci :** TiO<sub>2</sub>, fotokatalisis, radiasi UV, kinetika

### INTRODUCTION

Photocatalytic processes over metal oxide semiconductor materials have been gaining serious attention among the scientists since 1970[1,2]. The process based on the strong oxidative power of photogenerated holes on the photocatalyst surface becomes an excellent

alternative solution for the detoxification of those organic pollutants, in both air[3-6] and water[2,7-12]. When TiO<sub>2</sub> is illuminated with ultraviolet (UV) light of  $\lambda < 390$  nm, an electron is promoted from the valence band to the conduction band of the semiconductor to give an

electron/hole pair[11]. These holes play a major role by reacting with water molecules or  $\text{OH}^-$  groups on the semiconductor surface to produce hydroxyl radicals. The hydroxyl radical is a powerful oxidizing agent and attacks the adsorbed organic pollutants resulting usually in their complete oxidation to  $\text{CO}_2$ .

$\text{TiO}_2$  has been widely proven to have a high photocatalytic activity and chemical stability. Moreover, the film-type semiconducting photocatalysts offer the practical benefits that are not available with the powdered ones[13-16]. The film form requires no post-treatment removal/separation procedures which the powdered form requires if it is used in a suspension reactor. These removal/separation procedures are difficult and expensive, which means extra running costs of the plant. However, some workers have investigated several methods to immobilize the photocatalysts on various supports, including quartz[9,10], glasses[12-15], silica[16-21], stainless steel[10,12], titanium metal[12] titanium alloy[12], polymers, clays, surfactant vesicles, micelles, and sand.

In this work, we have prepared  $\text{TiO}_2$  from  $\text{TiCl}_4$  and  $\text{Ti}(\text{OPr})_4$  as the starting materials and the commercially available  $\text{TiO}_2$  from Merck as reference. The procedures for the preparation of the  $\text{TiO}_2$ , both powder-type and film-type were based on the references published in recent year[13,19-21].

The photocatalytic activities were measured in the photodegradation of gaseous acetaldehyde carried out in the batch reactor, using ambient air with approximately 55-60% relative humidity and at room temperature of  $25^\circ\text{C}$ . Batch reactors are used primarily to determine rate law parameters for homogeneous reactions. This determination is usually achieved by measuring concentration as a function of time and then using either the differential or integral method of data analysis to determine the reaction order,  $\alpha$ , and specific reaction rate,  $k$ .

## EXPERIMENTAL

### Materials

All chemicals used were reagent grade. Most of them were purchased from Merck, such as acetaldehyde,  $\text{TiO}_2$ ,  $\text{TiCl}_4$ , and polyethylene glycol (PEG). Other chemicals,  $\text{Ti}(\text{OPr})_4$  and tetraethylorthosilicate (TEOS) were purchased from Aldrich. A soda lime glass ( $25\text{ mm} \times 75\text{ mm} \times 1\text{ mm}$ ) was used as a support substrate for the film-type  $\text{TiO}_2$ . The light sources used were black-light-type lamps (five 10 W lamps).

### Preparing $\text{TiO}_2$ Powder from $\text{TiCl}_4$

$\text{TiCl}_4$  was hydrolyzed in an aqueous sodium carbonate solution to give a titanium hydroxide solution. After being filtered and washed, the resultant was

dispersed by adding nitric acid to yield a paint-like sol. The formed sol was then autoclaved for about an hour at  $120^\circ\text{C}$  and 10 atm pressure. To obtain the powdered form, the sol was dried at  $140^\circ\text{C}$  in air for 4 hours.

### Preparing $\text{TiO}_2$ Powder from $\text{Ti}(\text{OPr})_4$

$\text{Ti}(\text{OPr})_4$  was added slowly to an ethanol solution while being stirred. The suspension was then mixed with *n*-hexane. After being filtered, the absorbate was dried at  $110\text{-}120^\circ\text{C}$  for an hour and then calcined at  $400^\circ\text{C}$  for an hour.

### Preparing $\text{TiO}_2$ Film Over $\text{SiO}_2$ Layer

#### $\text{SiO}_2$ Coating

TEOS was diluted in a methanol solution while being stirred at approximately  $0^\circ\text{C}$  for 10 min. After being refluxed for an hour, the TEOS solution was then 50% evaporated. The solution was ready for the coating of soda lime plate by using a dip-coating method. The withdrawal speed used was  $60\text{ mm/min}$  repeated  $40 \times$ , and the plate was sintered at  $400^\circ\text{C}$  for an hour after each  $10 \times$  of coatings.

#### $\text{TiO}_2$ Coating

The  $\text{TiO}_2$  solution was made by adding a 10% wt of  $\text{TiO}_2$  powder to an ethanol solution. Using the same dip-coating method, the soda lime plate was coated for  $10 \times$  followed by sintering at  $400^\circ\text{C}$  for an hour.

### Photoactivity Examination

The photocatalytic activity of the photocatalysts was investigated by measuring the change in concentration of gas-phase acetaldehyde as a function of irradiation time. The photoreactor vessel used was made of pyrex glass, with a volume of  $1000\text{ cm}^3$ , shown schematically in Fig. 1. The UV intensity of  $0.6\text{ mW/cm}^2$  for each lamp was used. For the examination of the powder-type  $\text{TiO}_2$ , about 1.0 g of  $\text{TiO}_2$  powder was spread evenly on the soda lime plate with the same surface area

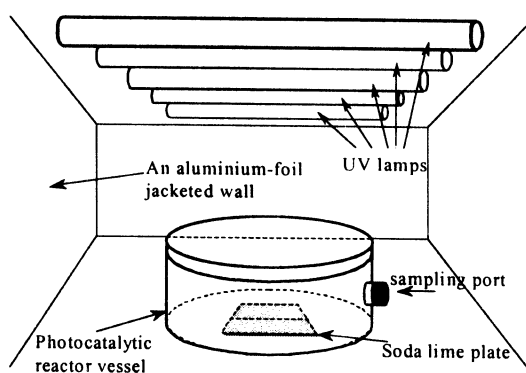


Fig. 1. A Scheme of photocatalytic reactor used for the photodegradation of gaseous acetaldehyde.

(about 37.5 cm<sup>2</sup> area). The plate was placed in the reaction vessel described above.

Saturated gaseous acetaldehyde was injected into the vessel through the sampling port. The irradiation was started after the equilibrium between the gaseous and the adsorbed acetaldehyde was reached (as ascertained by monitoring the concentration chromatographically about every 12 min). The gas chromatograph used was a Shimadzu Model GC-8A equipped with 2 m Porapak-Q column, with thermal conductivity detectors, and helium as the carrier gas.

All of the experiments were carried out at room temperature, with ambient air (relative humidity of about 55-60%).

## RESULTS AND DISCUSSION

### Adsorption in the Dark

The adsorption properties of gas-phase acetaldehyde on Merck powder, TiCl<sub>4</sub> powder and Ti(OPr)<sub>4</sub> powder were analyzed in terms of the Langmuir isotherm

$$\Theta = \frac{C_{ads}}{C_{max}} = \frac{K C_{eq}}{1 + K C_{eq}} \quad (1)$$

where  $\Theta$  is the surface coverage,  $C_{ads}$  is the surface concentration of adsorbed molecules,  $C_{max}$  is the maximum surface concentration available for the adsorbate,  $K$  is the adsorption equilibrium constant, and  $C_{eq}$  is the equilibrium concentration of the adsorbing species.

### Kinetic Analysis of Acetaldehyde Photodegradation

The quantitative kinetic analysis for acetaldehyde degradation were based on the rate constant  $k$ , which is independent of the concentrations used. Presently, in photocatalytic reactions,  $k$  is almost independent of temperature because of the photoactivation process and only depends on the radiant flux and on the reaction mechanism. The Langmuir-Hinshelwood (L-H) kinetic model was used in the assumption that the Langmuir adsorption isotherm is valid for the surface reaction. The rate  $R$  of a unimolecular surface reaction will be proportional to the coverage  $\Theta$ , as described in the following equation :

$$R = k \Theta = \frac{k K C_{eq}}{1 + K C_{eq}} \quad (2)$$

where  $k$  is the apparent first-order reaction rate constant. Since the initial concentration is low, ( $C_0 = 500$

ppmv), the term  $K C_{eq}$  in the denominator can be neglected with respect to unity and the rate becomes the apparent first-order

$$R = -dC/dt = k K C_{eq} = k_a C \quad (3)$$

where  $k_a$  is the apparent rate constant of the pseudo-first-order. Integrating the rate equation will give :

$$\ln(C_0/C) = k_a t \quad (4)$$

### Effect of Initial Concentration on the Photocatalytic Kinetics

The high or low initial concentration determines whether the acetaldehyde oxidation proceeded initially with first-order or zero-order reaction kinetics. When the initial concentration of acetaldehyde is relatively high, the number of the adsorbed acetaldehyde molecules on the TiO<sub>2</sub> surface will be much larger than the photogenerated holes on the catalytic surface of TiO<sub>2</sub>, thus decreasing the role of these holes in oxidizing the adsorbed molecules. Because these holes were trapped in the adsorbed molecules more likely than that in the water molecules or hydroxyl ions, so the formation of hydroxyl radicals does not fast enough compared to the recombination of electrons and holes at the interface. At this condition, the charge separation of electron/hole pairs becomes the rate limiting, thus the reaction proceeded with nearly zero-order kinetics. After sometime, these holes are separated back again from the electrons and can in turn oxidize the acetaldehyde molecules and the reaction proceeded further with first-order reaction kinetics. However, in this case, most of the adsorbed acetaldehyde molecules should be oxidized to acetic acid.

Conversely, when the initial concentration of acetaldehyde is relatively low, the number of the holes photoproduced on the TiO<sub>2</sub> surface is much larger the number of acetaldehyde molecules adsorbed, the proportion of direct oxidative conversion to CO<sub>2</sub> might increase. The mass transfer of acetaldehyde from

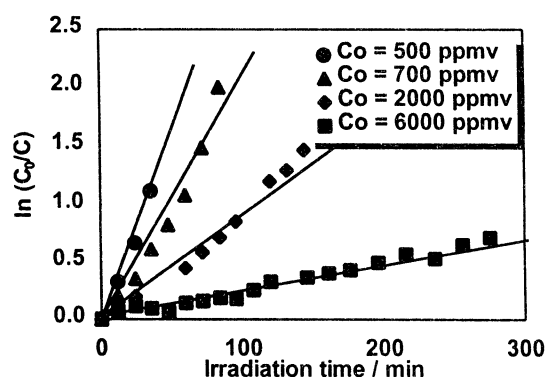


Fig. 2. Linear transforms  $\ln(C_0/C)$  as a function of irradiation time for photodegradation of acetaldehyde with Merck powder catalyst under UV intensity of 3.0 mW/cm<sup>2</sup>.

gas-phase into adsorbed phase becomes the rate limiting, thus the reaction proceeded with approximately first-order reaction kinetics.

Fig. 2 shows plots of the linear transforms  $\ln(C_0/C) = k_a t$  with the apparent slopes  $k_a$  of 0.0297, 0.0204, 0.0095, and  $0.0024 \text{ min}^{-1}$  for acetaldehyde initial concentration  $C_0$  of 500, 700, 2000 and 6000 ppmv, respectively. The plot of these slopes as a function of irradiation time can be described in Fig. 3.

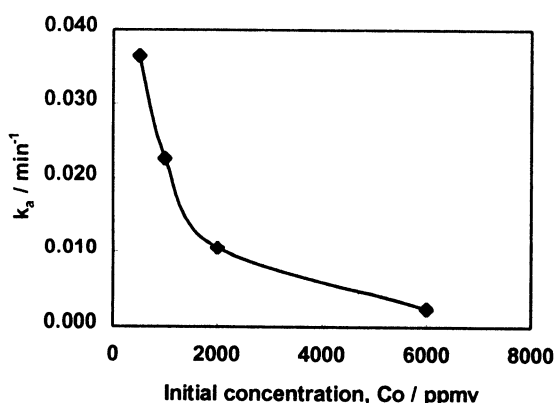


Fig. 3. Plot of pseudo-first-order reaction rate constant  $k_a$  vs. initial concentration  $C_0$  for photodegradation of acetaldehyde with Merck powder catalyst under UV intensity of  $3.0 \text{ mW/cm}^2$ .

It shows that the rate constant  $k_a$  decreases with increasing initial concentration of acetaldehyde  $C_0$ . The plot also shows that for  $C_0 < 2000 \text{ ppmv}$ , the slope of decreasing  $k$  is sharper than that for  $C_0 > 2000 \text{ ppmv}$ , which means for a relatively low  $C_0$ , a minor change in  $C_0$  gives a major effect to  $k_a$ . As previously explained above, when the mass transfer becomes the rate limiting, the reaction rate is much higher than that when the charge separation becomes the rate limiting. For a very high initial concentration ( $C_0 \gg \gg$ ), the changes in  $C_0$  becomes insignificant to the rate constant  $k_a$ .

### Effect of Light Intensity on the Photocatalytic Kinetics

The light intensity determines the number of incident photons while the photocatalytic process proceeds. The photo-nic flux increases with increasing light intensity. Under strong UV intensity, the acetic acid as an intermediate species will undergo further oxidation to  $\text{CO}_2$ .

Fig. 4(a) shows clearly that the higher the UV intensity, the shorter the time needed for the acetaldehyde degradation. A combination of a highly active photocatalyst, low initial concentration of acetaldehyde and high UV intensity results in an excellent photocatalytic performance of this  $\text{TiO}_2$  semiconductor catalyst. Acetaldehyde was completely oxidized within less than an hour after irradiation. For the

given conditions, the acetaldehyde degradation rate has been shown to parallel the  $\text{CO}_2$  production rate, as most of the acetaldehyde molecules were directly oxidized to  $\text{CO}_2$ . The reactions were approximately first-order, as shown by the linear transforms  $\ln(C_0/C) = k_a t$  in Fig 4(b). The rate constant  $k_a$  values for the Merck powder,  $\text{Ti}(\text{OPr})_4$  powder and  $\text{TiCl}_4$  powder were  $0.0297$ ,  $0.0184$ , and  $0.0117 \text{ min}^{-1}$ , respectively.

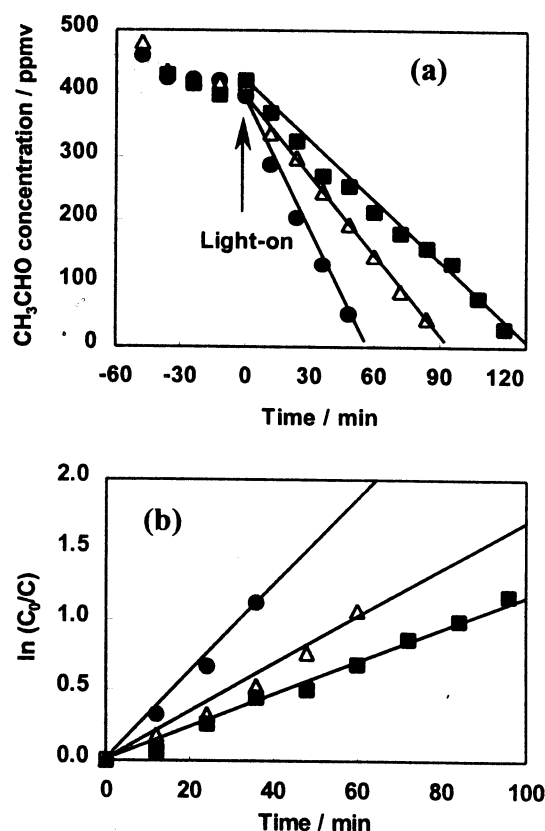


Fig. 4. Plots of (a) acetaldehyde concentration and (b) linear transforms  $\ln(C_0/C)$  versus irradiation time for photodegradation of acetaldehyde with Merck powder under UV intensities of  $3.0$  (●),  $1.8$  (Δ), and  $0.6 \text{ mW/cm}^2$  (■)

### Comparison of Photocatalytic Kinetics of the Different $\text{TiO}_2$ Powders

Three semiconductor catalysts in the powdered form were prepared for photoactivity examination in photodegradative oxidation of gaseous acetaldehyde at constant initial concentration. The photocatalytic activity of Merck powder was higher than the  $\text{TiO}_2$  prepared from  $\text{TiCl}_4$  and  $\text{Ti}(\text{OPr})_4$ . As shown in Fig. 5, the acetaldehyde degradation rate for Merck powder was much faster than the other two  $\text{TiO}_2$  powder.

The apparent first-order rate constants  $k_a$  of the photocatalysts in Fig. 5 were in the following order :

$$\text{TiO}_2 (\text{Merck}) < \text{TiO}_2 (\text{Ti}(\text{OPr})_4) < \text{TiO}_2 (\text{TiCl}_4)$$

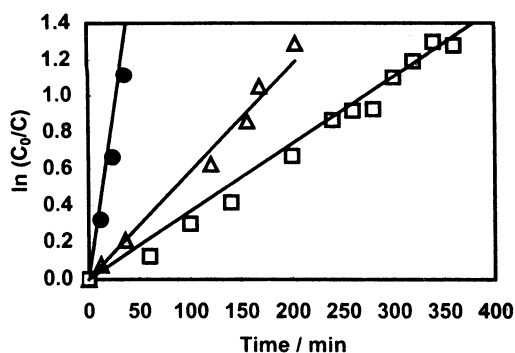


Fig. 5. Plots of linear transforms  $\ln(C_0/C)$  versus irradiation time for photodegradation of acetaldehyde with Merck powder (●),  $\text{Ti(OPr)}_4$  powder (Δ), and  $\text{TiCl}_4$  powder (□) under UV irradiation of  $3.0 \text{ mW/cm}^2$  intensity.

The high photoactivity of Merck powder was due to the extremely high purity powder (99.99%), unlike the other two  $\text{TiO}_2$  powders which were contaminated by impurities while preparing the catalysts with certain mixing processes. It was considered that the presence of impurities in  $\text{Ti(OPr)}_4$  and  $\text{TiCl}_4$  powders resulted in the decrease of band gap of the  $\text{TiO}_2$  particles, which leads the electron-hole recombination more likely to occur.

### Comparison of Photocatalytic Kinetics of the Different Shape $\text{TiO}_2$ Photocatalysts

Based on the catalyst shape, the powder and the film, an illuminated  $\text{TiO}_2$  photocatalysts were found to have different photoactivity. In this connection, for the purpose of photoactivity examination, the  $\text{TiO}_2$  from Merck and  $\text{TiO}_2$  prepared from  $\text{Ti(OPr)}_4$  were used.  $\text{TiO}_2$  from Merck was compared for the powder and the sintered film (no  $\text{SiO}_2$ -coating), while the  $\text{TiO}_2$  from  $\text{Ti(OPr)}_4$  was compared for the powder, the sintered film, and the  $\text{SiO}_2$ -coated film.

Fig. 6 shows that for the  $\text{TiO}_2$  prepared from  $\text{Ti(OPr)}_4$ , the  $\text{SiO}_2$ -coated film was found more active than the powder and the sintered film. Although the rate constants are similar, the amount of  $\text{TiO}_2$  in the film was much less than that in the powder sample used. Thus, if the rate constant is normalized to the weight of catalyst, the value for the film will be higher than that for the powder. The  $k_a$  values for the  $\text{SiO}_2$ -coated film, the sintered film and the powder were  $0.0090$ ,  $0.0021$ , and  $0.0061 \text{ min}^{-1}$ , respectively.

It was observed that the plot for  $\text{SiO}_2$ -coated  $\text{Ti(OPr)}_4$  film was not linear, and therefore indicating not the first-order kinetic. The plot showed linear after 60 min of irradiation time, so this means that the reaction did not proceed initially with first-order kinetics, but with zero-order kinetics. The same phenomenon was also observed for the Merck film, as shown in Fig. 7. One of the possible reasons is that the amount of  $\text{TiO}_2$  in the film form was

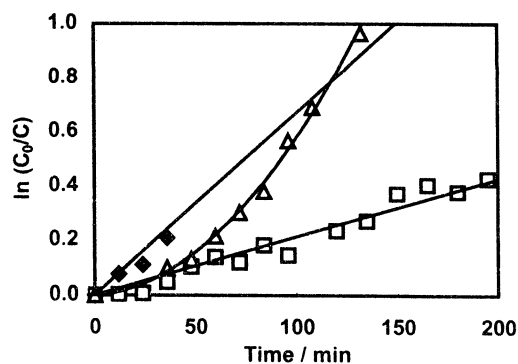


Fig. 6. Plots of linear transforms  $\ln(C_0/C)$  versus irradiation time for photodegradation of acetaldehyde with  $\text{Ti(OPr)}_4$  powder (◆),  $\text{SiO}_2$ -coated  $\text{Ti(OPr)}_4$  film (Δ), and sintered  $\text{Ti(OPr)}_4$  film (□) under UV irradiation of  $3.0 \text{ mW/cm}^2$  intensity.

much less than that in the powdered ones. So, for the given experiment conditions, the initial concentration of 500 ppmv was actually relatively high for the film form with respect to the mass of catalyst used.

The less active sintered film compared to the more active  $\text{SiO}_2$ -coated film can be attributed to the presence of cationic impurities on the  $\text{TiO}_2$  surface. The cations emerged as a consequence of the heat treatment while preparing the sintered film, for example the  $400^\circ\text{C}$  calcination. It is considered that the cations were diffused from the soda lime layer to the  $\text{TiO}_2$  layer.<sup>[10]</sup> These cations were responsible for the fast electron/hole recombination, and thus decreasing the quantum efficiency of the whole photocatalytic process. For soda lime substrate, the emerging cations are  $\text{K}^+$  and  $\text{Na}^+$ . However, the  $\text{SiO}_2$ -coated film was covered with the silica layer which held the diffusion of  $\text{Na}^+$  to the  $\text{TiO}_2$  layer, thus indicating more inert and stable at high temperature while calcined at  $400^\circ\text{C}$ . Therefore, the titania layer was free from the contamination of cationic impurities.

For the highly active  $\text{TiO}_2$  from Merck, apparently it showed the similar tendency to the  $\text{TiO}_2$  prepared from  $\text{Ti(OPr)}_4$ . The sintered film prepared from Merck powder was found to have lower activity than the

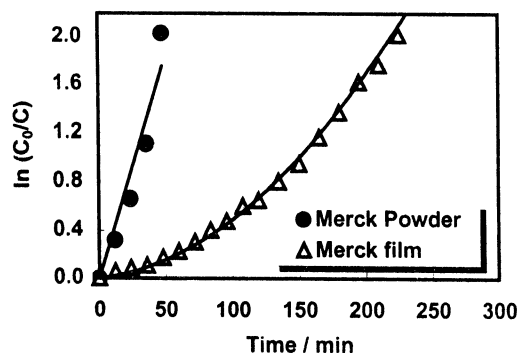


Fig. 7. Plots of linear transforms  $\ln(C_0/C)$  versus irradiation time for photodegradation of acetaldehyde with Merck powder (●) and film (Δ) under UV intensity of  $3.0 \text{ mW/cm}^2$ .

powder itself. Indeed, as previously explained, it is considered that the film prepared without an  $\text{SiO}_2$ -coating was contaminated with cationic impurities, as they were diffused to the titania layer. The plots of linear transforms  $\ln(C_0/C)$  vs. irradiation time for both Merck powder and film can be described in Fig. 7.

## CONCLUSIONS

The experiments on photocatalytic degradation of gaseous acetaldehyde with semiconductor catalyst  $\text{TiO}_2$  have yielded some major conclusions as follows:

- For a relatively low initial concentration, the reactions proceeded with approximately first-order reaction kinetics, where the mass transfer became the rate limiting.
- For a relatively high initial concentration, the reactions proceeded initially with nearly zero-order reaction kinetics where the charge separation became the rate limiting, and continued with first-order reaction kinetics after certain concentration was reached.
- The higher the UV intensity, the less the time needed for a complete photo-degradation of acetaldehyde.
- The photocatalytic activity of Merck powder was higher than that of  $\text{TiO}_2$  prepared from  $\text{Ti}(\text{OPr})_4$  and  $\text{TiCl}_4$ , with the rate constant  $k_a$  values of  $0.0297 \text{ min}^{-1}$  for  $C_0$  of 500 ppmv.
- The photocatalytic activity of  $\text{SiO}_2$ -coated  $\text{Ti}(\text{OPr})_4$  film was higher than that of film and powdered ones, with the rate constant  $k_a$  values of  $0.0090 \text{ min}^{-1}$  for  $C_0$  of 500 ppmv.

## ACKNOWLEDGEMENTS

This paper is a part of the results of research cooperation between Material Technology Center (BPPT) and FTUI. We thank Indonesia Toray Science Foundation (ITSF) for financial support during this work.

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