PHOTOCATALYTIC KINETICS OF GASEOUS ACETALDEHYDE DEGRADATION ON LOW INTENSITY ULTRA VIOLET IRRADIATED TiO$_2$

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ABSTRACT

PHOTOCATALYTIC KINETICS OF GASEOUS ACETALDEHYDE DEGRADATION ON LOW INTENSITY ULTRA VIOLET IRRADIATED TiO$_2$. The kinetics of photocatalytic degradation of gaseous acetaldehyde with semiconductor catalyst TiO$_2$, was studied. The experiment was carried out using TiO$_2$ photocatalyst prepared from titanium tetrachloride (TiCl$_4$) and titanium(IV) isoproxide (Ti(OR)$_4$) as the starting materials. Commerically available highly active TiO$_2$ from Merck was used for purposes of comparison. The TiO$_2$ films were prepared on soda lime plates and an SiO$_2$-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($C/C_0$) 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$_2$ film photocatalyst supported on soda lime plate shown lower photocatalytic activity than the powder one, however, when the films were coated on SiO$_2$-coated soda lime plate, photocatalytic activity of the resulting film increased and even higher than that of the powder form.

Key words: TiO$_2$, photocatalytic, UV radiation, kinetic.

ABSTRAK


Kata kunci: TiO$_2$, 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[7-12]. When TiO$_2$ 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
electrou/hole pair\textsuperscript{[11]}. These holes play a major role by reacting with water molecules or OH\textsuperscript{-} groups on the semiconducting surface to produce hydroxyl radicals. The hydroxyl radical is a powerful oxi-dizing agent and attacks the adsorbed orga-nic pollutants resulting usually in their complete oxidation to CO\textsubscript{2}.

Ti\textsubscript{2}O\textsubscript{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\textsuperscript{[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\textsuperscript{[9,10]}, glasses\textsuperscript{[12-15]}, silica\textsuperscript{[16-21]}, stainless steel\textsuperscript{[10,12]}, titanium metal\textsuperscript{[12]}, titanium alloy\textsuperscript{[12]}, poly-mers, clays, surfactant vesicles, micelles, and sand.

In this work, we have prepared TiO\textsubscript{2} from TiCl\textsubscript{4} and Ti(OPr)\textsubscript{4} as the starting materials and the commercially available TiO\textsubscript{2} from Merck as reference. The procedures for the preparation of the TiO\textsubscript{2}, both powder-type and film-type were based on the references published in recent years\textsuperscript{[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\°C. Batch reactors are used primarily to determine reaction 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, TiO\textsubscript{2}, TiCl\textsubscript{4}, and polyethylene glycol (PEG). Other chemicals, Ti(OPr)\textsubscript{4} and tetraethylorthosilicate (TEOS) were purchased from Aldrich. A soda lime glass (25 mm $\times$ 75 mm $\times$ 1 mm) was used as a support substrate for the film-type TiO\textsubscript{2}. The light sources used were black-light-type lamps (five 10 W lamps).

**Preparing TiO\textsubscript{2} Powder from TiCl\textsubscript{4}**

TiCl\textsubscript{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\°C and 10 atm pressure. To obtain the powdered form, the sol was dried at 140\°C in air for 4 hours.

**Preparing TiO\textsubscript{2} Film Over SiO\textsubscript{2} Layer**

**SiO\textsubscript{2} Coating**

TEOS was diluted in a methanol solution while being stirred at approximately 0\°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 mm/min repeated 10 times, and the plate was sintered at 400\°C for an hour after each 10$\times$ of coatings.

**TiO\textsubscript{2} Coating**

The TiO\textsubscript{2} solution was made by adding a 10\% wt of TiO\textsubscript{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\°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 cm\textsuperscript{3}, shown schematically in Fig. 1. The UV intensity of 0.6 mW/cm\textsuperscript{2} for each lamp was used. For the examination of the powder-type TiO\textsubscript{2}, about 1.0 g of TiO\textsubscript{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.](image-url)
(about 37.5 cm² 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, TiCl₄ powder and Ti₃O₅Pr₃ powder were analyzed in terms of the Langmuir isotherm

\[ \Theta = \frac{C_{ads}}{C_{max}} = \frac{K C_{eq}}{1 + K C_{eq}} \]  

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 Photo-degradation

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:

\[ R = k_1 \Theta = \frac{k K C_{eq}}{1 + K C_{eq}} \]  

where \( k_1 \) is the apparent first-order reaction rate constant.

Since the initial concentration is low, \( (C_o = 500 \) ppmv), the term \( K C_{eq} \) in the denominator can be neglected with respect to unity and the rate becomes the apparent first-order

\[ R = -\frac{dC}{dT} = k K C_{eq} = k_1 C \]  

where \( k_1 \) is the apparent rate constant of the pseudo-first-order. Integrating the rate equation will give:

\[ \ln\left(\frac{C}{C_0}\right) = k_1 t \]  

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 TiO₂ surface will be much larger than the photogenerated holes on the catalytic surface of TiO₂, 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 TiO₂ surface is much larger the number of acetaldehyde molecules adsorbed, the proportion of direct oxidative conversion to CO₂ might increase. The mass transfer of acetaldehyde from

![Fig. 2. Linear transforms ln(C/C) as a function of irradiation time for photodegradation of acetaldehyde with Merck powder catalyst under UV intensity of 3.0 mW/cm²](image)
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 $\ln(C_t/C) = k_t t$ with the apparent slopes $k_a$ of 0.0297, 0.0204, 0.0095, and 0.0024 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.

![Graph showing $k_a$ vs. initial concentration, $C_0$, for photodegradation of acetaldehyde with Merck powder catalyst under UV intensity of 3.0 mW/cm$^2$.](image)

**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 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 $C_0 < 2000$ ppmv, the slope of decreasing $k_a$ is sharper than that for $C_0 > 2000$ 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 CO$_2$.

![Graph showing CH$_3$CHO concentration vs. Time for photoirradiation of acetaldehyde with Merck powder under UV intensities of 3.0 (x), 1.8 (A), and 0.6 mW/cm$^2$ (■).](image)

**Fig. 4**. Plots of (a) acetaldehyde concentration and (b) linear transforms $\ln(C_t/C)$ versus irradiation time for photodegradation of acetaldehyde with Merck powder under UV intensities of 3.0 (x), 1.8 (A), and 0.6 mW/cm$^2$ (■).

**Comparison of Photocatalytic Kinetics of the Different 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 photo-catalytic activity of Merck powder was higher than the TiO$_2$ prepared from TiCl$_4$ and Ti(OPr)$_4$. As shown in Fig. 5, the acetaldehyde degradation rate for Merck powder was much faster than the other two TiO$_2$ powder.

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

$$\text{TiO}_2 (\text{Merck}) < \text{TiO}_2 (\text{Ti(OPr)}_4) < \text{TiO}_2 (\text{TiCl}_4)$$
The high photoactivity of Merck powder was due to the extremely high purity powder (99.99%), unlike the other two TiO₂ powders which were contaminated by impurities while preparing the catalysts with certain mixing processes. It was considered that the presence of impurities in Ti(OPr)₄ and TiCl₄ powders resulted in the decrease of band gap of the TiO₂ particles, which leads the electron-hole recombination more likely to occur.

Comparison of Photocatalytic Kinetics of the Different Shape TiO₂ Photocatalysts

Based on the catalyst shape, the powder and the film, an illuminated TiO₂ photocatalysts were found to have different photoactivity. In this connection, for the purpose of photoactivity examination, the TiO₂ from Merck and TiO₂ prepared from Ti(OPr)₄ were used. TiO₂ from Merck was compared for the powder and the sintered film (no SiO₂-coating), while the TiO₂ from Ti(OPr)₄ was compared for the powder, the sintered film, and the SiO₂-coated film.

Fig. 6 shows that for the TiO₂ prepared from Ti(OPr)₄, the SiO₂-coated film was found more active than the powder and the sintered film. Although the rate constants are similar, the amount of TiO₂ 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 values for the SiO₂-coated film, the sintered film and the powder were 0.0090, 0.0021, and 0.0061 min⁻¹, respectively.

It was observed that the plot for SiO₂-coated 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 TiO₂ in the film form was much less than that in the powdered ones. So, for the given experiment conditions, the initial concen-tration 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 SiO₂-coated film can be attributed to the presence of cationic impurities on the TiO₂ surface. The cations emerged as a consequence of the heat treatment while preparing the sintered film, for example the 400°C calcination. It is considered that the cations were diffused from the soda lime layer to the TiO₂ layer. 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 K⁺ and Na⁺. However, the SiO₂-coated film was covered with the silica layer which held the diffusion of Na⁺ to the TiO₂ layer, thus indicating more inert and stable at high temperature while calcined at 400°C. Therefore, the titania layer was free from the contamination of cationic impurities.

For the highly active TiO₂ from Merck, apparently it showed the similar tendency to the TiO₂ prepared from Ti(OPr)₄. The sintered film prepared from Merck powder was found to have lower activity than the
CONCLUSIONS

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

- For a relatively low initial concentra-tion, the reactions proceeded with approximately first-order reaction kinetics, where the mass transfer became the rate limiting.

- For a relatively high initial concentra-tion, 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 TiO$_2$ prepared from Ti(OR)$_4$ and TiCl$_4$, with the rate constant $k_0$ values of 0.0297 min$^{-1}$ for $C_0$ of 500 ppm.

- The photocatalytic activity of SiO$_2$-coated Ti(OR)$_4$ film was higher than that of film and powdered ones, with the rate constant $k_0$ values of 0.0090 min$^{-1}$ for $C_0$ of 500 ppm.

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REFERENCES


