Photocatalytic decomposition of acetaldehyde gas on TiO$_2$-SiO$_2$ thin film photocatalyst — A kinetic analysis

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TiO$_2$-SiO$_2$ thin film photocatalysts with 5 (TF95/5) and 10 w/w% (TF90/10) SiO$_2$ contents have been prepared via sol-gel method. Characterization using X-ray diffractometer and field emission scanning electron microscopy is performed to investigate the effect of SiO$_2$ doping on the TiO$_2$ thin film’s physico-chemical properties. The photocatalytic performance of the thin films is evaluated using the degradation of acetaldehyde gas at various initial concentrations under fixed intensity UV irradiation. A Langmuir-Hinshelwood kinetic model is used to analyze the kinetics of the photocatalytic reaction. It is found that the first order reaction rate constant ($k$) of the TF95/5 thin film photocatalyst (1.2438 µmol dm$^{-3}$ min$^{-1}$) is higher than that of TF90/10 thin film (0.3648 µmol dm$^{-3}$ min$^{-1}$). This is attributed to higher crystallinity of the TF95/5 thin film, resulting in more active charge carrier generation. However, TF90/10 thin film photocatalyst with smaller TiO$_2$ particles shows four times stronger adsorbability of acetaldehyde than TF95/5 due to its higher surface area.

Keywords: Acetaldehyde gas, Kinetic study, Sol-gel, TiO$_2$-SiO$_2$ photocatalyst, Thin film

Irradiated TiO$_2$ is one of the most powerful oxidants due to its high oxidizing potential. Chemical stability of TiO$_2$ towards aqueous and non-aqueous media makes TiO$_2$ an excellent photocatalyst for environmental protection. However, the application of TiO$_2$ powder as a photocatalyst brings many practical problems such as difficult separation of catalyst from its suspension after process completion, necessary to stir mixture during reaction, and aggregation of suspended particles for high concentration systems. Coating the photocatalyst on various functional substrates can eliminate problems encountered in powder systems. Unlike powder form, thin film form can prevent the scattering of light and enhance the transmittance of light, thus resulting in high reaction efficiency. It is also an inexpensive installation and can easily be recovered after photodegradation. Another advantage of thin film photocatalyst application is that the layer may be connected to an external power source to reduce the recombination of UV-activated electrons and holes; this also increases the efficiency of the catalyst. If a conductive material is used as the substrate, the catalyst film can be connected to an external potential to remove excited electrons and reduce electron-hole recombination, thereby significantly improving the process efficiency.

Recently, there has been increased interest in developing TiO$_2$ photocatalysts compositized with other semiconductors for better photoefficiency. Doping TiO$_2$ photocatalyst with another semiconductor material is an alternative approach to modify the surface of semiconductor colloids which can directly improve charge separation and minimize or even inhibit charge-carrier recombination. Several groups have developed this dual semiconductor systems or composite thin film photocatalyst, such as TiO$_2$/V$_2$O$_5$, TiO$_2$/SiO$_2$, TiO$_2$/ZrO$_2$, TiO$_2$/Al$_2$O$_3$, WO$_3$/TiO$_2$, and TiO$_2$/SnO$_2$. It is particular interesting to produce TiO$_2$-SiO$_2$ photocatalysts owing to the ability of SiO$_2$ in altering the physical and chemical properties (crystalline phase, grain size, surface hydroxyl content and transmittance) which can lead to a better photocatalytic activity. The addition of SiO$_2$ gives a suppressive effect on the grain growth of TiO$_2$ crystal. This effect is also found in TiO$_2$-SiO$_2$ thin film. SiO$_2$ can act as an absorbent and TiO$_2$ as a photocatalytic centre. The formation of Ti-O-Si gives more surface acidity sites that would take the form of stronger surface hydroxyl groups and absorb more water.

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molecules. Another researcher\textsuperscript{17} also supported the theory to describe acidity of TiO\textsubscript{2}/SiO\textsubscript{2} surface. Acidity enhancement of Si-O-Ti bonds at the SiO\textsubscript{2}/TiO\textsubscript{2} interfaces would induce a greater amount of hydroxyl groups on the film surface\textsuperscript{17}.

This paper reports study on the development and characterization of TiO\textsubscript{2}-SiO\textsubscript{2} thin film of 5 and 10 mol\% SiO\textsubscript{2} through sol-gel method. Its photocatalytic activity has been evaluated on the photocatalytic degradation of gaseous acetaldehyde. Acetaldehyde is selected as a representative of organic pollutant molecules due to its malodorous properties. It is well known as a strong respiratory irritant and toxicant. Multiple studies have reported photocatalytic degradation of gaseous acetaldehyde\textsuperscript{13,18,19}. Langmuir isotherm is used to analyze the adsorption property of the thin film photocatalyst. The kinetics of the photocatalytic reaction is analyzed using Langmuir-Hinshelwood (L-H) kinetic model. Besides, quantum yield of photocatalytic reaction is calculated to study the effect of various initial concentration of reactant on the photocatalytic reaction.

**Experimental Procedure**

**Reagents**

For synthesis of polytitanosiloxane (PTS) solution, titanium (di-isopropoxide) bis (acetyl-acetonate) (PTP) (Strem Chemicals, 75\%), tetraethoxysilane (TEOS) (Alfa Aesar, 98\%), methanol (SYSTERM, reagent grade) and hydrochloric acid (SYSTERM, 36\%) were used as received.

**Preparation of PTS coating solution**

The PTS solution was produced by stirring TEOS and 30 mL of methanol into the round-bottomed flask. Into this solution, a mixture of 6N HCl, distilled water and 30 mL methanol was added drop-wise by using disposable pipette with 10 min stirring process to hydrolyze the TEOS partially. The molar ratios of HCl/TEOS, H\textsubscript{2}O/TEOS and PTP/TEOS are summarized in Table 1. Then, the partially hydrolyzed TEOS was polymerized by adding PTP drop-wise. After the addition of PTP solution, the heating process was started and continued until the reflux temperature is reached (~74°C). The heating process was stopped after 10 min and finally PTS solution was obtained.

**Fabrication of TiO\textsubscript{2}-SiO\textsubscript{2} thin film**

For the synthesis of TiO\textsubscript{2}-SiO\textsubscript{2} thin film samples (TF95/5 and TF90/10), the soda lime glass substrate was carefully cleaned with acetone in ultrasonic bath and dried in drying oven. A spin coating machine, model WS-400B-6NPP/LITE from Laurell Technologies Corporation, was used to coat the PTS solution on the substrate. The spinning condition was fixed to obtain uniform distribution of PTS solution and control the formation of thin film thickness on the substrate. Then, wet gel thin film of TiO\textsubscript{2}-SiO\textsubscript{2} was dried at 200°C for 1 h in drying oven. The coating process was repeated several times to increase the thickness of the thin film. After finishing the coating and drying process, the thin film was calcined at 500°C for 7 h in air to obtain anatase crystal structure TiO\textsubscript{2}.

**Characterization**

The degree of crystallinity and the presence of anatase crystal structure of TiO\textsubscript{2}-SiO\textsubscript{2} thin film were characterized by using X-Ray diffractometer (XRD) (Shimadzu, XRD 6000) with copper K\textalpha\textsubscript{1} radiation. All samples were scanned between 20° and 50° with 2.00°/min scan rate. Scherer’s equation was used to measure the crystallite size of the particles. The results were compared with those by a nanoparticle sizer (Malvern Instruments, Zen 1600). Morphological analysis was conducted by using field emission scanning electron microscopy (FESEM) instrument (JEOL FESEM, JSM 6700F Series).

**Photocatalytic measurement**

Seven pieces of TiO\textsubscript{2}-SiO\textsubscript{2} thin film photocatalyst were placed in the airtight photoreactor vessel and their positions were fixed in order to have a constant UV intensity of 3.0 mW/cm\textsuperscript{2}. The thin film photocatalysts contribute to the apparent surface area of 131 cm\textsuperscript{2}. This vessel was placed under a UV reactor, equipped with UV black light (Hitachi, F20T9/BL). To measure the UV intensity, a digital UV meter (Solartech Inc., 5.0 UVA+B model) was used. Saturated acetaldehyde gas was injected into the vessel in the range of 1800-8000 ppmv.

The UV irradiation was conducted at ambient temperature after the equilibrium state between the

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO\textsubscript{2}, %</th>
<th>SiO\textsubscript{2}, %</th>
<th>PTP, mol</th>
<th>TEOS, mol</th>
<th>H\textsubscript{2}O/TEOS, mol ratio</th>
<th>HCl/TEOS, mol ratio</th>
<th>Methanol, mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>TF95/5</td>
<td>95</td>
<td>5</td>
<td>0.095</td>
<td>0.005</td>
<td>2</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td>TF90/10</td>
<td>90</td>
<td>10</td>
<td>0.090</td>
<td>0.010</td>
<td>2</td>
<td>0.1</td>
<td>30</td>
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gaseous and the adsorbed acetaldehyde was achieved (as determined by monitoring the concentration chromatographically about every 15 min). This equilibrium condition was achieved after 2 h injection of the gas into the vessel. Then, the vessel, which contained the TiO\textsubscript{2}-SiO\textsubscript{2} thin film photocatalyst, was placed under a UV reactor to start the irradiation of UV on the photocatalyst to degrade the injected acetaldehyde gas. The decrease in acetaldehyde concentration was measured using a gas chromatograph (Perkin Elmer, Clarus 500 model) equipped with the Column (Elite-PLOT Q), both with flame ionization detector (FID). The sampling under UV irradiation was done for 3 h after 2 h of equilibrium state. A nitrogen gas was used as the carrier gas. A methanizer was attached to the GC to convert the produced CO\textsubscript{2} to methane. The FID measurement of methane concentration represents the concentration of the CO\textsubscript{2} produced. The concentration measurement of CO\textsubscript{2} and acetic acid (CH\textsubscript{3}COOH) produced should be determined to evaluate the photocatalytic performance of the thin film photocatalyst by calculating the quantum yield of the photocatalytic reaction.

Results and Discussion

The XRD patterns of TiO\textsubscript{2}-SiO\textsubscript{2} thin films of TF95/5 and TF90/10 after 500°C calcinations for 7 h were recorded. Identification of the phase in the calcined thin films is achieved by comparing the obtained XRD patterns with PDF Card No. 21-1272 for TiO\textsubscript{2} with anatase crystal structure that appears at 25.3° in 2θ. No peaks other than those attributable to anatase were observed. From the peak broadening in the TF90/10 thin film’s pattern it is clear that the TF90/10 thin film has smaller TiO\textsubscript{2} particle size compared to that of TF95/5. This can be ascribed as the suppressive effect of SiO\textsubscript{2} on the crystal growth of TiO\textsubscript{2} particles. Since the atomic radii of Si atom is smaller than Ti, the TiO\textsubscript{2} particle experiences a contraction. Its crystal growth retards by the existence of Si atom. This occurrence corroborates with the smaller value of average crystal size (7 nm for TF90/10 and 16 nm for TF95/5 as calculated using Scherer’s equation) and supported by the nanosizer analysis (129 nm for TF90/10 versus 150 nm for TF95/5).

A small shift of the anatase peak to higher 2θ position (from 25.36 to 25.39 in 2θ) implying a change in particle size is observed as the content of SiO\textsubscript{2} increased. This peak shift also qualitatively shows that Si atom is substituted into the TiO\textsubscript{2} lattice. However, it can be seen that the TF95/5 thin film has higher crystallinity than that of TF90/10 thin film which could lead to more active charge carrier generation and thus give better photocatalytic activity.

As can be seen in Fig. 1, smaller particles of TiO\textsubscript{2} with spherical shape are observed on the TF90/10 thin film [Fig. 1(b)] compared to that of TF95/5 thin film [Fig. 1(a)] as corroborated with the XRD analysis. It may possibly be due to the presence of SiO\textsubscript{2} matrix that leads to the suppressive effect on the crystal growth of TiO\textsubscript{2} grains. As a consequence, the TF90/10 thin film has much lower crystallinity than the TF95/5 thin film.

Photocatalytic measurement

Figure 2 shows semilogarithmic plots of the decrease in concentration of acetaldehyde gas with the increase in irradiation time (semilogarithmic plot), as it undergoes a photocatalytic process using TF95/5 thin film photocatalyst. Various initial concentrations of acetaldehyde gas are applied for the photocatalytic experiment under UV illumination of 3.0 mW/cm\textsuperscript{2} intensity. About 120 min after the injection of the reactant gas into the vessel, adsorption equilibrium is
reached and then the irradiation starts. Just after being irradiated to the UV illumination, the photocatalytic reactions obey apparent first-order kinetics as shown by the apparent exponential decay of initial decreases in acetaldehyde concentrations.

It is observed that the TF95/5 thin film photocatalyst has higher rate in degrading the acetaldehyde compared to the TF90/10 film. Thus, it can be said that the drastic decrease in concentration of acetaldehyde is correlated to the highly crystalline phase of TF95/5 thin film photocatalyst. It is established that higher crystallinity in TiO$_2$ could lead to more active of charge carrier generation. Thus, more oxidizing and reducing agents are produced to decompose the organic compound adsorbed on the surface of thin film photocatalyst. However, this judgment is only based on the empirical value which is obtained directly from the slope of the graph and excludes the effect of adsorption process.

TF90/10 thin film photocatalyst shows higher decrease in concentration of acetaldehyde gas in dark adsorption. It may be attributed to the small particles size of TiO$_2$ on the surface of TF90/10 thin film photocatalyst, resulting in the higher surface area for gas molecules adsorption. The adsorption property depends on the crystallite size. The adsorption constant increases as the crystallite size decreases since it relates to the interfacial tension on particle size. Since TF90/10 thin film photocatalyst has higher adsorption property, the gas molecules are saturated on the surface of thin film photocatalyst, resulting in the interruption of photons absorption. Therefore, charge carrier generation is reduced, leading to the slower rate of acetaldehyde degradation.

Figure 3 shows carbon dioxide production from the photocatalytic degradation of acetaldehyde gas at various initial concentrations of the gas over the TF90/10 thin film photocatalyst. In early period of the photocatalytic degradation, the highest rate of CO$_2$ production is found for 5000 ppmv and 5500 ppmv. Finally, however, the photocatalytic degradation of 8000 ppmv acetaldehyde shows the highest rate in CO$_2$ production. Presumably, when the concentration of acetaldehyde molecules on the photocatalyst surface is too high, most of the degraded acetaldehyde is converted to acetic acid, leaving smaller portion of acetaldehyde for its direct oxidation to CO$_2$. However, when the concentration of acetaldehyde decreases, its oxidation to CO$_2$ occurs predominantly due to higher concentration of photons relative to acetaldehyde molecules on the film surface.

Dependences of quantum yield on initial concentration of acetaldehyde gas

Several variables have been introduced to evaluate the photocatalytic performance of the photocatalyst. The most common are overall quantum yield ($\bar{O}$) which can be defined as the number of molecules of a given product formed or number of molecules of a given reactant consumed per photon of light at a given wavelength, that is absorbed by the photocatalyst. Apparent quantum yield is always used to measure the capacity of the light absorbed by assuming that all the light is absorbed during process.

The efficiency can also be measured as the yield of a particular product if there are several products formed from the photocatalytic reaction. In the
quantum yield calculation, it should be noted that initial rate of acetaldehyde disappearance and CO₂ production are used. In principle, the photocatalytic reaction of acetaldehyde with the TiO₂-SiO₂ thin film photocatalyst proceeds as described below:

\[
\text{CH}_3\text{CHO} \text{(ads)} + \text{H}_2\text{O} + 2h^+ \rightarrow \text{CH}_3\text{COOH} \text{(ads)} + 2\text{H}^+ \quad \text{... (1)}
\]

and

\[
\text{CH}_3\text{CHO} \text{(ads)} + 3\text{H}_2\text{O} + 10h^+ \rightarrow 2\text{CO}_2 + 10\text{H}^+ \quad \text{... (2)}
\]

Two different situations can exist in the photocatalysis reaction as described by the Eqs (1) and (2). When the number of molecules adsorbed on the thin film photocatalyst surface is much larger than the number of photons adsorbed by the acetaldehyde molecules mostly oxidized to acetic acid [Eq. (1)]. On the other hand, the direct conversion of acetaldehyde molecules to the CO₂ happens when the number of the holes photogenerated on the thin film photocatalyst surface is much larger than the number of acetaldehyde molecules adsorbed [Eq. (2)].

Representative plots (Fig. 4) shows the effect of initial concentration of acetaldehyde on quantum yield of the photocatalytic reaction for thin films TF 95/5 and TF 90/10. In both cases, it can be observed that the quantum yield of the photocatalytic reaction increases directly with the increase in initial concentration of acetaldehyde from 1800 ppmv to 5500 ppmv. Indeed, in a photocatalytic experiment with a high UV intensity, a larger number of photons adsorbed by the thin film photocatalyst suggest an increase in the number of holes photogenerated on the thin film surface. Although the adsorbed acetaldehyde gas molecules increase, the holes photogenerated on the thin film photocatalyst surface are still adequate for the gas molecules degradation. In this correlation, the quantum yield of intermediate and end-product produced by the photocatalytic reaction rapidly increases.

The quantum yield is drastically decreased as the initial concentration of the acetaldehyde gas increases up to 8000 ppmv. In order to clarify this finding, it is noteworthy to mention that the saturation of acetaldehyde gas molecules on the surface of the thin film photocatalyst becomes an obstacle for the irradiated photons to reach and stimulate the TiO₂ particles for the photocatalytic reaction. Therefore, the photons absorption by the surface of the thin film photocatalyst reduces and this contributed to the slower degradation rate.

According to Fig. 4, a remarkable quantum yield value is obtained by the photocatalytic reaction of the TF95/5 thin film photocatalyst on the acetaldehyde gas degradation. Its quantum yield exceeds than the unity when the initial concentration of the acetaldehyde gas is 5000 ppmv and 5500 ppmv. This finding could be deduced that the photocatalytic reaction is not exclusively mediated by hole-generated hydroxyl radicals, but it may involve a carbonyl-radical-mediated chain reaction mechanism as reported before.

**Adsorption isotherm analysis**

In order to investigate the adsorption property of gas molecules on the thin film photocatalyst surface during dark adsorption, the saturated acetaldehyde vapour is injected into a sealed and air-filled container. Gas chromatograph is used to measure the decrease in acetaldehyde concentration via adsorption onto the thin film photocatalyst surface. The equilibrium state is reached after about 2 h of injecting the gas into the photoreactor vessel. The adsorbed concentration (C_ads) is calculated by subtracting the equilibrium concentration (C_eq) from the initial concentration (C_o). Langmuir isotherm model has been used by plotting the graph of \( I/C_{ads} \) versus \( I/C_{eq} \) and the Langmuir adsorption parameter is used to calculate the adsorption constant of the TiO₂-SiO₂ thin film photocatalyst, as shown by the following Langmuir equation:
The Langmuir isotherm parameters $C_{\text{max}}$ and $K_{\text{ads}}$ are determined using linear least-square analysis of the plots $1/C_{\text{ads}}$ versus $1/C_{\text{eq}}$. It is found that the $K_{\text{ads}}$ value of TF90/10 thin film photocatalyst (0.0095 dm$^{-3}$ µmol$^{-1}$) is much higher than that of TF95/5 thin film (0.0026 dm$^{-3}$ µmol$^{-1}$). This indicates that the adsorbability for acetaldehyde is higher for TF90/10 thin film photocatalyst than for TF95/5 thin film photocatalyst. As revealed by XRD analysis, the TiO$_2$ particles on the surface of the TF90/10 thin film photocatalyst are around two times smaller than that of TF95/5 thin film photocatalyst and significantly contributes to the better adsorption of reactant gas molecules. It has been established that smaller particle size of TiO$_2$ has higher surface area for gas molecules adsorption. This smaller size of the TiO$_2$ particles on the TF90/10 thin film photocatalyst is obtained due to the suppressive effect of SiO$_2$ on the crystal growth of TiO$_2$ grains. Hence, it can be concluded that an optimum content of SiO$_2$ dopant can enhance the adsorption property of the thin film photocatalyst by giving higher surface area for gas molecules adsorption.

### Kinetic analysis using Langmuir-Hinshelwood kinetic model

Several kinetic models describe the mechanism of the photocatalytic oxidation reaction with as simple pseudo first order reaction kinetic model, resulting in the application of the L-H law. The pseudo first order reaction kinetics is expressed as:

$$\text{Rate} = R = \frac{dG}{dt} = k \theta$$

The L-H rate expression considers the relationship between the photocatalytic reaction rates and the concentration of the reactant gas. Besides, the L-H equation also includes the key role of adsorption constant ($K_{L-H}$) on kinetics, assuming that adsorption and desorption kinetics is faster than the photochemical reaction. From the equation, the plots of the reciprocal of the initial degradation rate ($1/R$) is related to the reciprocal of the equilibrium concentration of the reactant gas ($1/C_{eq}$) to get the L-H parameters as shown by the following equation:

$$\frac{1}{R} = \left(\frac{1}{kK_{L-H}}\right) \left(\frac{1}{C_{eq}}\right) + \frac{1}{k}$$

where $k$ is the apparent first order reaction rate constant, $K$ is an adsorption equilibrium constant and both are the L-H parameters. The value $K$ here is denoted as $K_{L-H}$ to show that this adsorption equilibrium constant is obtained using L-H kinetic model.

In determining the L-H kinetic parameters ($k$ and $K_{L-H}$), the plots of the reciprocal of the initial degradation rate ($1/R$) vs. the reciprocal of the equilibrium concentration of acetaldehyde ($1/C_{eq}$) is an essential. The value of $R$ is calculated by subtracting the concentration after 15 min of UV irradiation ($C_{15\text{min}}$) from the equilibrium concentration ($C_{eq}$). Then, the values of $k$ and $K_{L-H}$ are obtained from the slope and y-intercept of the plots using linear least-square analysis.

If the plots show a good linearity, the treatment using the L-H model is appropriate for the photocatalytic activity of acetaldehyde in contact with...
the thin film photocatalyst. The 1/k is the intercept value of the y-axis and used to obtain the k value. The value of $K_{L-H}$ is determined using the slope value which is equal to the 1/k. The parameter k reflects the photocatalytic activity of a photocatalyst in a particular photocatalytic reaction. The $K_{L-H}$ is a parameter that shows the strength of adsorption.

Figure 5 shows the L-H parameter values for the apparent first order reaction rate constant (k) and adsorption equilibrium constant ($K_{L-H}$) \( k = 1.2438 \mu\text{mol dm}^{-3} \text{min}^{-1} \) & \( 0.3648 \mu\text{mol dm}^{-3} \text{min}^{-1} \) for TF95/5 and TF90/10 and $K_{L-H} = 0.0029 \text{dm}^{-3} \mu\text{mol}^{-1} \) & \( 0.0137 \text{dm}^{-3} \mu\text{mol}^{-1} \) for TF95/5 and TF90/10 respectively. It can be seen that the apparent first order reaction rate constant of TF95/5 thin film photocatalyst is higher than that of TF90/10 thin film photocatalyst with a factor of 3.4. By comparing the $K_{L-H}$ and $K_{ads}$ values, it is also worth to note that the values for the adsorption equilibrium constant for TF95/5 (0.029 dm$^{-3}$ µmol$^{-1}$) and TF90/10 (0.0137 dm$^{-3}$ µmol$^{-1}$) obtained from the kinetic analysis are in good agreement with those obtained from the adsorption analysis (0.0026 dm$^{-3}$ µmol$^{-1}$ for TF95/5 and 0.0095 dm$^{-3}$ µmol$^{-1}$ for TF90/10), thus confirming the validity of the L-H fitting.

The reason for the high photocatalytic activity of the TF95/5 thin film photocatalyst in degrading the acetaldehyde gas can be elucidated by the difference in the crystallinity between the TF95/5 and TF90/10 thin film photocatalysts. From the XRD analysis, it is confirmed that the TF95/5 photocatalyst has higher crystallinity than that of the TF90/10 thin film photocatalyst. It has been established that higher crystallinity of the TiO$_2$ thin film photocatalyst will lead to the more charge carrier produced.

A remarkable high crystallinity of thin film photocatalyst will result in bigger size of the TiO$_2$ particles on the thin film surface. In this connection, it is important to note that the bigger size of TiO$_2$ particles lead to the increase in a number of charge carrier recombination centres due to its lower band gap energy. However, in our work, the TF95/5 thin film photocatalyst has higher crystallinity without a noticeable increase in particle size. For this reason, higher crystallinity of TF95/5 thin film photocatalyst is determined as the major factor controlling and giving higher photocatalytic activity in degrading the acetaldehyde molecules.

Furthermore, a large difference between the degradation rate of TF95/5 and TF90/10 thin film photocatalysts can be attributed to the different content of SiO$_2$ dopant in both thin film samples. The formation of Ti-O-Si absorbs more water molecules to generate the hydroxyl radicals and enhances its photocatalytic activity. However, higher content of SiO$_2$ dopant in the TF90/10 thin film photocatalyst is expected to reduce its photocatalytic activity. This result suggests that an excess of SiO$_2$ on the TF90/10 thin film photocatalyst leads to less TiO$_2$ on the surface of the thin film photocatalyst. Less TiO$_2$ content means fewer number of photocatalytic centres. Indeed, this excess content of SiO$_2$ would hinder the TiO$_2$ particles to interact with organic molecules and decelerate the photocatalytic activity.

Our results also suggest that the slower degradation rate of TF90/10 thin film photocatalyst on degrading the acetaldehyde gas may be ascribed to its better adsorption property. Referring to the adsorption equilibrium constant, it is observed that larger number of acetaldehyde gas molecules can be adsorbed by the TF90/10 thin film photocatalyst. The more saturated acetaldehyde gas molecules on the surface of the TF90/10 thin film photocatalyst are likely to shift kinetics from first-order to zero-order kinetics, leading to the slower rate of photocatalytic degradation.

The quantum yield values of TF95/5 and TF90/10 thin film photocatalysts imply that the higher quantum yield for the formation of acetic acid is obtained for both thin film photocatalyst samples. This judgment leads us to the conclusion that larger formation of acetic acid on the surface of thin film photocatalyst could reduce the rate of photocatalytic activity for TF90/10 thin film photocatalyst. On the other hand, in the case of TF95/5 thin film photocatalyst, this
occurrence may not be happened due to the production of more charge carrier, as it has higher crystallinity that can compensate the saturated molecules of acetic acid.

Conclusion

TiO$_2$-SiO$_2$ thin film photocatalyst has been successfully developed via sol-gel method with two different content of SiO$_2$ doped, namely 5\% (TF95/5) and 10\% (TF 90/10). From the characterization steps, it is found that TiO$_2$-SiO$_2$ thin film photocatalyst with higher content of SiO$_2$ (TF90/10) has smaller particle size with spherical shape. However, it has lower crystallinity compared to that of TF95/5 thin film photocatalyst. From the adsorption analysis, it can be concluded that the TF90/10 thin film photocatalyst has better adsorption property as it has smaller size of TiO$_2$ particle for larger adsorption of gas molecules. The photocatalytic activity of the thin film is evaluated in terms of acetaldehyde gas degradation under a constant UV light intensity. TF95/5 thin film photocatalyst shows much higher photocatalytic activity than TF90/10, due to its high crystallinity.

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