Korean J. Chem. Eng., **25**(5), 1232-1238 (2008)

Photocatalytic degradation of methylene blue and acetaldehyde by TiO_2/glaze coated porous red clay tile

Seung-Joon Yoo*, Se-Il Lee*, Dong-Heui Kwak*,†, Kwang-Gil Kim, Kyung-Jun Hwang***, Jae-Wook Lee***, Un-Yeon Hwang****, Hyung-Sang Park*****, and Jong-Ok Kim********

*Faculty of Environmental and Chemical Engineering, Seonam University, 720 Gwangchi-dong, Namwon 590-711, Korea
**Faculty of Design, Seonam University, 720 Gwangchi-dong, Namwon 590-711, Korea
***Department of Chemical Engineering, Chosun University, 375, Seosuk-dong, Dong-gu, Gwangju 501-759, Korea
****Department of Bio-Chemical Engineering, Dongyang University, Punggi, Yeongju 750-711, Korea
*****Department of Chemical Engineering, Sogang University, 1 Sinsoo-dong, Mapo-gu, Seoul 121-742, Korea
******Inwol Ceramics Company, 21-13, Joonggunri, Inwol, Namwon 590-842, Korea

(*Received 14 April 2008 • accepted 21 June 2008*)

Abstract−Nanosized TiO_2 sol synthesized by sol-gel method was successfully coated on the porous red clay tile (PRC tile) with micrometer sized pores. PRC tile was first coated with a low-firing glaze (glaze-coated PRC tile) and then TiO_2 sol was coated on the glaze layer. A low-fired glaze was prepared at various blending ratios with frit and feldspar, and a blending ratio glazed at 700 °C was selected as an optimum condition. Then TiO_2 sol synthesized from TTIP was dip-coated on the glazed layer (TiO_2/glaze-coated PRC tile), and it was calcined again at 500 °C. Here, these optimum calcination temperatures were selected to derive a strong bonding by a partial sintering between TiO_2 sol particles and glaze layer. Photocatalytic activity on the TiO_2/glaze-coated PRC tile was evaluated by the extent of photocatalytic degradation of methylene blue and acetaldehyde. Methylene blue with the high concentration of 150 mg/*l* on the surface of TiO_2/glaze-coated PRC tile was almost photodegraded within 5 hours under the condition of average UV intensity of 0.275 mW/cm^2, while no photodegradation reaction of methylene blue occurred on the glaze-coated PRC tile without TiO_2. Another photocatalytic activity was also evaluated by measuring the extent of photocatalytic degradation of gaseous acetaldehyde. The photodegradation efficiency in TiO_2/glaze-coated PRC tile showed about 77% photocatalytic degradation of acetaldehyde from 45,480 mg/*l* to 10,536 mg/*l* after the UV irradiation of 14 hours, but only about 16% in the case of the glaze-coated PRC tile.

Key words: Porous Red Clay Tile, TiO_2, Glaze, Methylene Blue, Acetaldehyde

INTRODUCTION

Photocatalysts can efficiently decompose organic contaminants with their strong oxidizing ability which is generated when the photocatalysts are irradiated by UV light. TiO_2 is one of the representative semiconductors. Among the TiO_2 crystalline phases, the band gap energy of rutile is 3.00 eV and that of anatase is 3.23 eV. This means that UV light (wavelength<387 nm) can excite anatase TiO_2 to generate conduction band electron and valence band hole (e^-/h^+) pairs. When UV light is irradiated to the TiO_2 layer, the conduction band electrons and valence band holes can then migrate to the surface and participate in interfacial oxidation-reduction reactions. The oxidative degradation of an organic pollutant is attributed to indirect reactions at the positive hole where the adsorbed water or hydroxyl radicals (-OH) react with the pollutant molecule [1]. However, TiO_2 mainly displays high activity when it is irradiated by UV light shorter than 400 nm. The natural sunlight contains about 3-5% of UV light [2].

Currently, many products are being developed by applying the self cleaning ability of TiO_2 including the deodorizing, anti-bacterial, anti-fouling, anti-fogging agents, and the sick house syndrome prevention agent [3-8].

Above all, the development of high activated TiO_2 material is essential to derive the indoor or outdoor photocatalytic degradation under the condition of natural sunlight.

The red clay tile has many functions such as excellent adsorption ability, humidity conditioning, temperature storage, temperature conditioning and anti-bacteria [9], but the surface of the tile is easily polluted by means of high adsorption ability. To manufacture PRC tile with a self-cleaning ability and a preventive function of sick house syndrome, the TiO_2 layer was coated on the surface of PRC tile pre-coated with a glaze layer. At this time, a glaze layer was coated as a buffer layer because the PRC tile has micrometric pore sizes but TiO_2 sol has nanometer-sized particles. That is why the TiO_2 sol particles are difficult to coat directly on the surface of PRC tile. Therefore, a low-firing glaze layer was first coated on the surface of the PRC tile as a buffer before coating the photocatalytic TiO_2 sol to prevent the nanometric TiO_2 sol particles from penetrating into micrometric pores. Of course, the glaze layer blocks the pores of the PRC tile, but the PRC tile has many of functions like the radiation of far-IR ray, temperature storage function, and anti-bacterial as before except the adsorption ability.

Unlike previous studies that have been evaluating photocatalytic effects by coating a thin layer of TiO_2 particles using soda-lime glass or quartz [10-15], we conducted our research using PRC tile with many large pore sizes, without using soda-lime glass or quartz.

EXPERIMENTAL

---

† To whom correspondence should be addressed.
E-mail: kwak124@hanmail.net

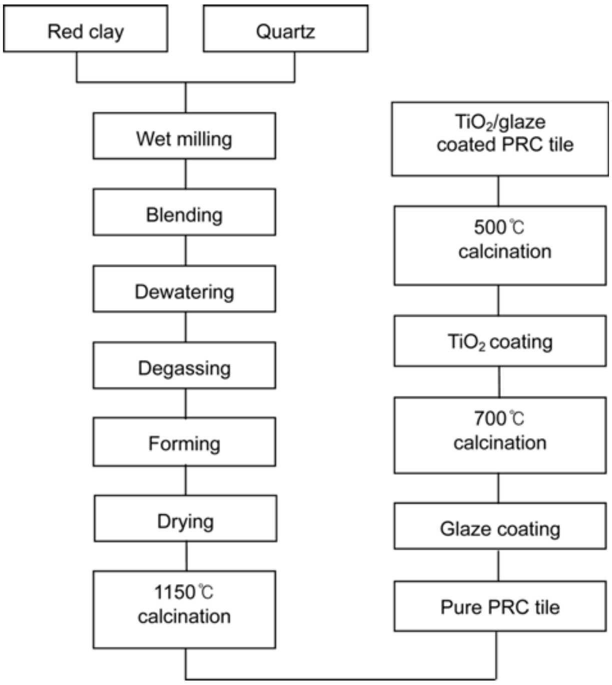


Fig. 1. Experimental flowchart for TiO_2/glaze-coated tile preparation.

1. Materials and Methods

Based on the results of past research [9], the PRC tile was manufactured through milling, blending, degassing, forming and drying stages with 90% red clay and 10% quartz and calcined at 1,150 °C for 1 hour as shown in Fig. 1. Blended raw materials were milled by wet milling. The milled raw materials were dehydrated and degassed. The dehydrated body was pressed by a forming machine into the shape of tile. The tile thus formed was dried for 3 days and calcined for 1 hour at 1,150 °C.

Using a titanium tetra-isopropoxide (TTIP, >98%, Junsei) as a starting material, the transparent nanosized TiO_2 sol was synthesized by hydrolysis and poly/condensation at 45 °C for 30 minutes, aged for 10 min at the same condition, and then added 0.19 mol HNO_3/mol Ti (HNO_3, 60%, Daejung) as a peptizing agent. These synthesized nanometer sized TiO_2 sol particles easily penetrate into the tile pores of micrometer size. Accordingly, TiO_2 sol is impossible to coat directly on the surface of red clay tile. Therefore, a low-firing glaze layer was first coated on the surface of the PRC tile as a buffer to block up the pores of tile and was calcined for 1 hour at 700 °C. At this time, the calcination temperature for the glaze layer was determined experimentally to derive a high bonding ability by a sintering between the glaze layer and the TiO_2 particles.

The low-fired glaze was blended with the components of frit and feldspar. The component ratios of frit and feldspar were controlled from 100 : 0 to 50 : 50, and then the glazing temperatures were experimentally obtained according to the component ratios.

Finally, the synthesized transparent TiO_2 sol was coated on the glaze-coated PRC tile, then dried and calcined for 1 hour at 500 °C. Here, the calcination temperature for TiO_2 layer was selected to derive a strong bonding by a partial sintering between the glaze layer and the TiO_2 particles and also to convert TiO_2 particles into an anatase crystalline phase with the highest activity among the various crystalline phases of TiO_2 [16].

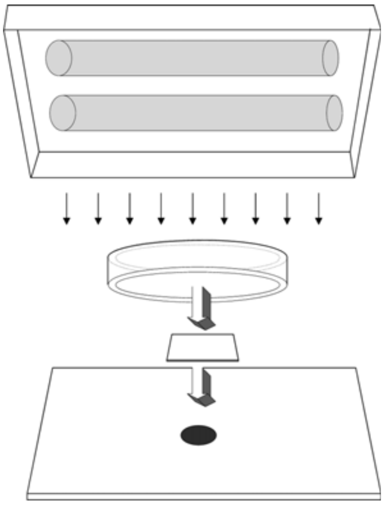


Fig. 2. Schematic diagram for photocatalytic degradation of methylene blue.

2. Analysis

The photocatalytic activity of the TiO_2 layers was evaluated by photocatalytic decoloration of methylene blue ($C_{16}H_{18}ClN_3S\cdot 3H_2O$, Aldrich) and by the degraded extent of gaseous acetaldehyde since many studies have already been conducted by measuring the photodegradative oxidation of gaseous acetaldehyde (CH_3CHO, >99.5%, CARLO-ERBA) as a standard test reaction [17-25].

For a semi-qualitative analysis, the photodegradation ability of the final manufactured TiO_2/glaze-coated PRC tile was evaluated by the decoloring of methylene blue on the TiO_2 layer in order to observe a visual change. For an indicator, methylene blue with light resistance was used as a blue indicator and the concentration for the analysis was 30 mg/*l*. In this photodegradation analysis of the TiO_2 coated PRC tile, however, the methylene blue was concentrated about 5 times to 150 mg/*l* in order to distinguish the color change easily because the color of PRC tile was dark brown. Fig. 2 shows the schematic diagram of the experimental apparatus for photocatalytic degradation of methylene blue. The UV light source was irradiated at the tile surface with 10×10 cm^2 dimension at 25 °C temperature and maintained at an interval of 10 cm between the light source and the tile. All UV irradiations were performed by using two black light UV-A lamps (F20T10/BLB, Dimension 580 mm (length)×32.5 mm (diameter), lamp current 0.360 A, UV output 3.6 W, 315-400 nm (UV-A), Sankyo Denki (Japan)), with an irradiance of 0.2752 mW/cm^2 (min. 0.2446 mW/cm^2, max. 0.2821 mW/cm^2) when placed directly above the tile under test. At this time, UV intensity was measured by a photo-radiometer (HD2302.0 model, Delta Ohm, Italy). The photodegradation reactions of methylene blue were confirmed by a sensuous test on two samples of the common white tile and the PRC tile. Here, the white tile was used to clearly distinguish the degree of decoloring of methylene blue by photodegradation.

For a quantitative analysis, the photodegradation ability of the TiO_2/glaze-coated PRC tile was also evaluated by the extent of degradation of gaseous acetaldehyde. The acetaldehyde was analyzed

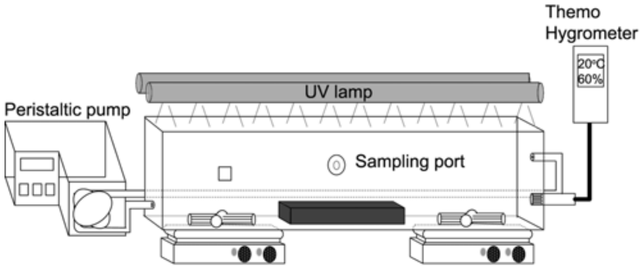


Fig. 3. Schematic diagram of photocatalytic degradation reactor.

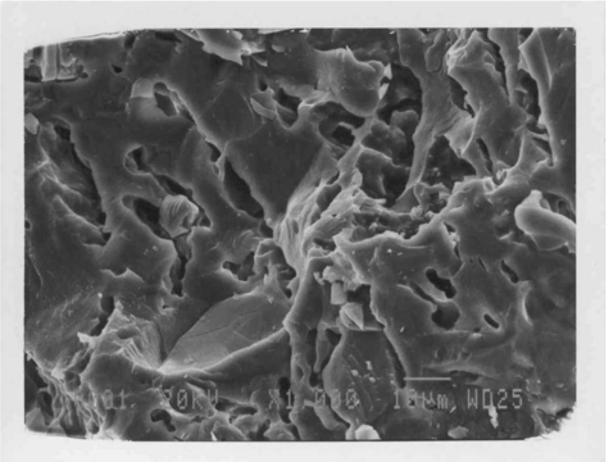
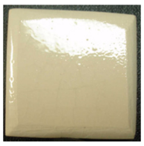
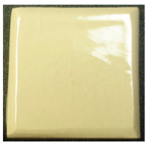
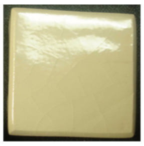
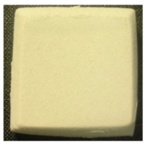
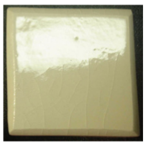
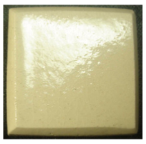
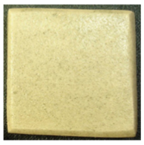
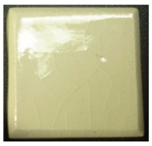


Fig. 4. SEM Photograph of the red clay tile surface.

by a photocatalytic reactor shown in Fig. 3. The analytical condition for efficiency of photocatalytic degradation was as follows: the photoreactor with UV light source: the distance between test sample and light source, 10 cm; light source 360 nm BLB lamps; the dimensions of the photocatalytic reactor 57.5(L)×18.0(W)×6.5(H) cm^3; temperature 25 °C; and relative humidity 60%. In this analytical condition, the TiO_2/glaze-coated on the PRC tile with a 15×15 cm^2 dimension was put on in the photocatalytic reactor, and the acetaldehyde was injected into the photocatalytic reactor with 6.728 L inner volume by gas syringe. The initial concentration of acetaldehyde gas in the reactor was analyzed to 45,480 mg/*l* on a gas chromatographer. The photocatalytic ability was analyzed according to

Table 1. Initial glazing temperatures according to blending ratios of frit to feldspar

Temp. (°C) / Blending ratios	600 °C	700 °C	800 °C	900 °C	1,000 °C	Initial glazing temp. (°C)
frit(100): feldspar(0)						700
frit(90): feldspar(10)						700
frit(80): feldspar(20)						900
frit(70): feldspar(30)						900
frit(60): feldspar(40)						900
frit(50): feldspar(50)						1,000

the photodegradation time under the illumination of the UV light. Acetaldehyde gas was sampled out with a gas syringe according to photodegradation times and analyzed on a gas chromatographer. A Hewlett-Packard HP 5890 gas chromatographer equipped with a flame ionization detector (FID) and a 50 m×0.20 mm×0.3 μm HP-FFAP capillary column was used for analysis.

RESULTS AND DISCUSSION

The surface of PRC tile has many more pores than micrometers with various shapes as shown in Fig. 4. Therefore, it is impossible to coat nanosized TiO_2 sol directly on the surface of this red clay tile. So a low-firing glaze layer was first coated on the surface of the PRC tile as a buffer to block up the pores of tile in this study.

The key contribution of this study is the method of determining the glazing temperature of low-firing glaze. The calcination temperature for the buffer layer should be considered through the correlations between the buffer layer and the TiO_2 particles. The low-firing glaze was blended with the components of frit and feldspar. The blending ratios were controlled from 50 : 50 to frit only as shown in Table 1. The initial glazing temperatures according to each component ratios were changed as shown in Table 1. In this study, the best condition for the buffer layer was the blending ratio of 90 frit to 10 feldspar. If the initial glazing temperature is higher than 900 °C, there is no sintering between TiO_2 sol particles and the glaze layer after coating of TiO_2 sol. Since the TiO_2 layer is easy to detach from the glaze layer, the glaze is not appropriate for our purpose.

If the glazing temperature is lower than 700 °C, TiO_2 particles are swamped into the glaze layer because of the complete sintering between TiO_2 sol particles and the glaze layer. After all, the photocatalytic characterization by TiO_2 particles never appears. Based on the result listed in Table 1, we selected as an optimum condition for glaze layer a ratio of 90 to 10 (frit to feldspar) and the calcination temperature of 700 °C.

The PRC tile is exposed to the outdoor condition of well-irradiated natural sunlight, maximizing the use of ultraviolet wave in the sunlight. Therefore, manufacturing high activated TiO_2 sol is essential in increasing photocatalytic efficiency because ultraviolet wave is contained within the 3-5% of sunlight. For the synthesis of highly activated TiO_2 sol, the sol was synthesized to the most transparent and stable TiO_2 sol. Fig. 5 shows a field-emission transmission electron microscopy image (FE-TEM, Technai F20, Phillips) of TiO_2 sol particles synthesized by this experiment. The synthesized sol particles have polycrystalline phase and spherical shape of 3 nm size.

Fig. 6 represents X-ray diffraction patterns of TiO_2 sol particles peptized at 0.19 mol HNO_3/mol Ti according to the various calcination temperatures. A high anatase TiO_2 phase appeared at the con-

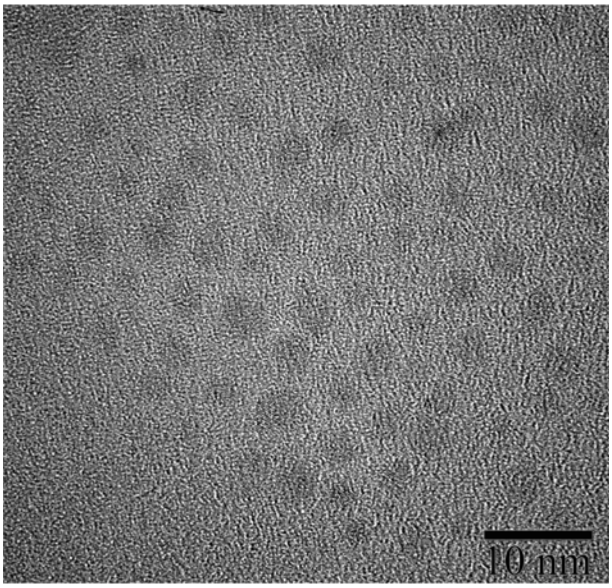


Fig. 5. TiO_2 sol particles synthesized by sol-gel method.

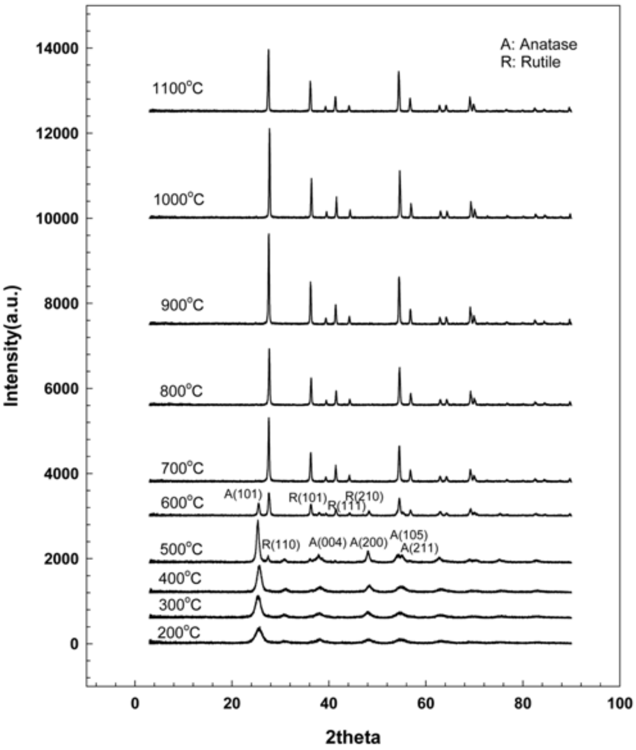


Fig. 6. XRD curves of TiO_2 according to calcination temperatures.

Fig. 7. TiO_2/glaze-coated PRC tile.

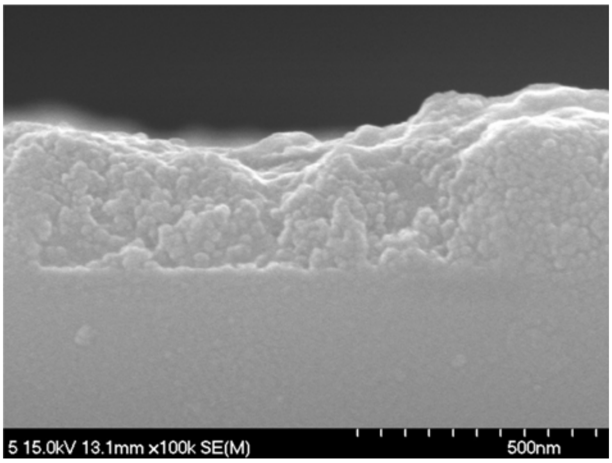


Fig. 8. Photograph of TiO_2 layer coated on the glaze layer.

Table 3. Photocatalytic degradation characterization of methylene blue on the PRC tile according to UV irradiation times

Time Type	1 hour	5 hours
Glaze only coated PRC tile		
TiO_2/glaze-coated PRC tile		

dition of 500 °C. On the other hand, at 600 °C, the anatase crystalline phase was slowly converted into a rutile crystalline phase. Accordingly, TiO_2 sol particle was calcined for 1 hour at 500 °C after the coating on the glaze layer because anatase is reported to exhibit the highest activity among the crystalline phases of TiO_2. Through these processes, the photoactive TiO_2/glaze-coated PRC tile was finally manufactured as shown in Fig. 7.

Fig. 8 shows the TiO_2 layer and the glaze layer coated on the PRC tile observed by field-emission scanning electron microscopy (FE-SEM, S-4700, Hitachi). The glaze layer has a dense structure, and the TiO_2 layer was coated on the glaze layer with a thickness of about 300 nm. An UV irradiated photoreactor system was manufactured to measure the degradation of methylene blue. At this time, the average UV intensity irradiated on the tile was analyzed to be 0.275 mW/cm^2 on a photo-radiometer. Methyl group in the methylene blue was dissolved by UV irradiation, transformed into thionine structure, and the native blue color of methylene blue itself disappeared finally [26].

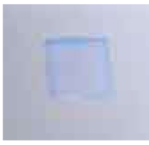
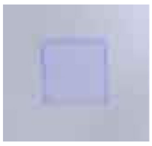
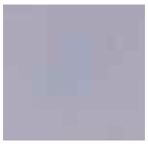
One of the most interesting aspects of TiO_2 is that the types of photochemistry responsible for photocatalysis and superhydrophilicity are completely different, even though both can occur simultaneously on the same surface [27]. In the case of superhydrophilic mechanism, a semiconductor photocatalyst is activated with UV irradiation in the photocatalytic processes. The activated photocatalyst promotes the formation of hydroxyl radicals, which in turn completely degrades the pollutants. In this experiment, as soon as a drop of the methylene blue solution falls into the TiO_2 layer, it is almost impossible to measure the contact angle by using a contact angle instrument. The result is shown at the initial condition in Table 2. Table 2 presents the result of photocatalytic degradation characterization of the methylene blue on the common white tile. Here, the methylene blue with a concentration of 30 mg/*l* on the TiO_2 coated on common white tile was completely degraded within 10 minutes after irradiation of UV. On the other hand, in the case of the pure white tile, the methylene blue was not degraded at all even after UV irradiation of 1 hour.

Table 3 presents the results of photocatalytic degradation characterization of the methylene blue on the TiO_2/glaze-coated PRC tile and the glaze-coated PRC tile. It was difficult to judge the color changes of methylene blue at the concentration of 30 mg/*l* which was dropped on the surface of the tile for the analysis of the photocatalytic ability because the PRC tile is reddish brown, which is darker than the color of the methylene blue. Therefore, the concentration of methylene blue was increased to 150 mg/*l* to induce a darker color.

As a result, the TiO_2/glaze-coated PRC tile was degraded of almost all the methylene blue after 5 hours, whereas the glaze-coated PRC tile did not show any characteristics of photocatalytic degradation at all.

Our experimental results led us to conclude that the self-clean-

Table 2. Photocatalytic degradation characterization of methylene blue on the white tile according to UV irradiation times

Time Type	0 min	5 min	10 min	30 min	60 min
Pure white tile					
TiO_2 coated white tile					

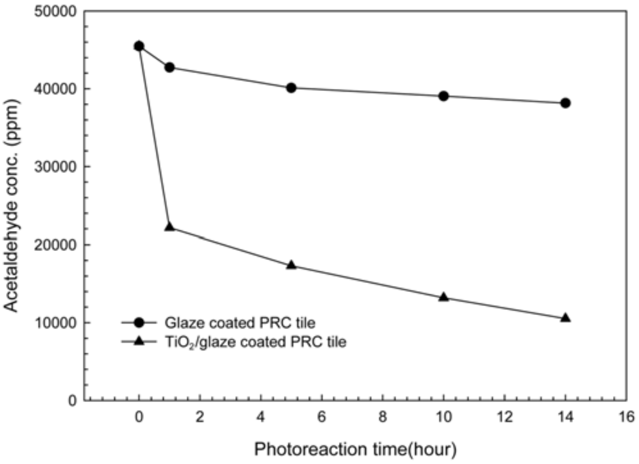


Fig. 9. Photocatalytic degradation efficiency of acetaldehyde on the TiO_2/glaze-coated PRC tile.

ing ability functioned effectively through photocatalysis and photoinduced hydrophilicity on the surface of the TiO_2/glaze-coated PRC tile, as reported in previous studies by other researchers [28-31]. The photoactive ability on the prepared TiO_2/glaze-coated PRC tile was also judged by the extent of photodegradation of the acetaldehyde gas because this has been considered a key molecule in understanding the photochemistry of larger carbonyl compounds. Fujishima et al. [32] have reported that acetaldehyde is degraded into CO_2, H_2O and O_2 by the photodegradation mechanism.

As a result of the analysis of the acetaldehyde gas by gas chromatographer, the initial acetaldehyde concentration showed an apparently exponential decay after the start of UV irradiation. The concentration of the gaseous acetaldehyde was decreased about 77% from the initial concentration of 45,480 mg/*l* to 10,536 mg/*l* after UV irradiation of 14 hours as shown in Fig. 9. On the other hand, in the case of glaze-coated PRC tile for a blank test, the acetaldehyde concentration decreased about 16% to 38,150 mg/*l* under the same condition of UV irradiation. Therefore, the photodegradation effect by TiO_2 layer appeared as 61%. At this time, the average UV intensity irradiated on the TiO_2/glaze-coated PRC tile was 0.275 mW/cm^2. This UV intensity is about 70% higher than the UV intensity of 0.162 mW/cm^2 existing in natural sunlight on sunny days in autumn (Namwon city, Republic of Korea).

CONCLUSIONS

Pure PRC tile has various functionalities, but the surface is easily polluted because of its porous pore structures and high adsorption ability. Therefore, we coated a photocatalytic TiO_2 sol on the PRC tile in order to provide a self-cleaning ability and an ability to prevent sick house syndrome on PRC tile. The nanosized TiO_2 sol was synthesized to the scale of about 3 nm by a hydrolysis and poly/condensation at 45 °C for 30 minutes, aged for 10min at the same condition, and then peptized by 0.19 mol HNO_3/mol Ti to obtain the most transparent nanosized TiO_2 sol. But the PRC tile has pore sizes of several tens micrometer scale. Therefore, the glaze was precoated as a buffer layer on the PRC tile and then the synthesized TiO_2 sol was coated on the surface of the glaze layer. At this time, these calcination temperatures were chosen experimentally to derive a strong bonding by a sintering between the glazed layer and the TiO_2 layer.

The photocatalytic activity of the manufactured TiO_2/glaze-coated PRC tile was estimated qualitatively by the photocatalytic degradation characterization of methylene blue. On the other hand, the glaze-coated PRC tile showed no photocatalytic ability. Yet, in the case of the TiO_2/glaze-coated PRC tile, methylene blue with a concentration of 150 mg/*l* was almost photodegraded within 5 hours under the UV intensity of 0.275 mW/cm^2.

For a quantitative analysis, the photocatalytic ability of the manufactured TiO_2/glaze-coated PRC tile was evaluated by measuring the extent of degradation of gaseous acetaldehyde that is causing the sick house syndrome. In the photocatalytic reactor, the TiO_2/glaze-coated PRC tile has decreased the concentration from 45,480 mg/*l* acetaldehyde to 10,536 mg/*l* within 5 hours.

This result shows that 77% acetaldehyde was degraded after 5 hours. On the other hand, in the case of the PRC tile coated only with glaze without TiO_2 sol, acetaldehyde was degraded only about 16% to 38,150 mg/*l* under the same condition of UV irradiation.

ACKNOWLEDGMENTS

The research was supported by the Small and Medium Business Administration of Republic of Korea.

REFERENCES

1. C. S. Turchi and D. F. Ollis, *J. Catal.*, **122**, 178 (1990).
2. S. Karvinen and R. J. Lamminmaki, *Solid State Sciences*, **5**, 1159 (2003).
3. Y. Paz and A. Heller, *J. Mater. Res.*, **12**, 2759 (1997).
4. T. Watanabe, A. Nakajima, R. Wang, M. Minabe, S. Koizumi, A. Fujishima and K. Hashimoto, *Thin Solid Films*, **351**, 260 (1999).
5. A. Nakajima, K. Hashimoto and T. Watanabe, *Langmuir*, **16**, 7044 (2000).
6. S. Hata, Y. Kai, I. Yamanaka, H. Oosaki, K. Hirota and S. Yamazaki, *JSAE Rev.*, **21**, 97 (2000).
7. J. Keleher, J. Bashant, N. Heldt, L. Johnson and Y. Li, *World J. Microbiol. Biotechn.*, **18**, 133 (2002).
8. G. Sivalingam, K. Nagaveni, M. S. Hedge and G. Mardras, *Appl. Catal. B: Environ.*, **45**, 23 (2003).
9. S. J. Yoo and J. O. Kim, Korean Patent 432590 (2004).
10. H. Yu, J. Yu and B. Cheng, *Catal. Commun*., **7**, 1000 (2006).
11. A. Mills, S. J. K. Lee and A. Lepre, *J. Photochem. Photobiol. A: Chem.*, **155**, 199 (2003).
12. H. Kobayashi, M. Takahashi and M. Kotani, *Chem. Phys. Lett.*, **349**, 376 (2001).
13. K. Shimizu, H. Imai, H. Hirashima and K. Tsukuma, *Thin Solid Films*, **351**, 220 (1999).
14. J. S. Chen, J. S. Kao, G. R. Lai and W. H. Wang, *Appl. Optics.*, **36**, 4403 (1997).
15. A. Mills, J. Wang and J. McGrady, *Phys. Chem. B*, **110**, 18324 (2006).
16. K. Kato, A. Tsuzuki, H. Taoda, Y. Torü and J. Katoutsugan, *Mater. Sci.*, **29**, 5911 (1994).
17. I. Sopyan, M. Watanabe, S. Murasawa, K. Hashimoto and A. Fujish-

ima, *J. Photochem. Photobiol. A: Chem.*, **98**, 79 (1996).

18. J. L. Falconer and K. A. Magrini-Bair, *J. Catal.*, **179**, 171 (1998).
19. A. Fujishima and D. A. Tryk, *Photoelectrical conversion*, in: K. Honda (Ed.), *Functionality of molecular systems*, Springer, Tokyo, **2**, 196 (1999).
20. E. Obuchi, T. Sakamoto and K. Nakano, *Chem. Eng. Sci.*, **54**, 1525 (1999).
21. M. C. Blount, D. H. Kim and J. L. Falconer, *Environ. Sci. Technol.*, **35**, 1988 (2001).
22. T. Sano, N. Negishi, K. Uchino, J. Tanaka, S. Matsuzawa and K. Takeuchi, *J. Photochem. Photobiol. A: Chem.*, **160**, 93 (2003).
23. T. Sano, N. Negishi, K. Takeuchi and S. Matsuzawa, *Solar Energy*, **77**, 543 (2004).
24. Y. Kurosaki and L. Yokoyama, *J. Phys. Chem. A*, **106**, 11415 (2002).
25. D. Chatterjee and S. Dasgupta, *J. Photochem. Photobiol. C: Photochem. Rev.*, **6**, 186 (2005).
26. T. Zhang, T. Oyama, S. Horikoshi, H. Hidaka, J. Zhao and N. Serpone, *Sol. Energ. Mat. Sol. C*, **73**, 287 (2002).
27. K. Huan, *Surf. Coat. Tech.*, **191**, 155 (2005).
28. M. Miyauchi, A. Nakajima, T. Watanabe and K. Hashmoto, *Chem. Mater.*, **14**, 4714 (2002).
29. J. F. Zhi, H. B. Wang and A. Fujishima, *Ind. Eng. Chem. Res.*, **41**, 726 (2002).
30. N. Sakai, A. Fujishima, T. Watanabe and K. Hashimoto, *J. Phys. Chem. B*, **107**, 1028 (2003).
31. X. T. Zhang, O. Sato, M. Taguchi, Y. Einaga, T. Murakami and A. Fujishima, *Chem. Mater.*, **17**, 696 (2005).
32. A. Fujishima, T. N. Rao and D. A. Tryk, *J. Photochem. Photobiol. C: Photochem. Rev.*, **1**, 1 (2000).