J. KOSAE Vol. 22, No. E 1 (2006) pp. 19~26
Journal of Korean Society for Atmospheric Environment

Photocatalytic Decomposition of Gaseous Acetaldehyde by Metal Loaded TiO_2 with Ozonation

Ki-Chul Cho* and Hyun-Gu Yeo[1)]

Department of Environmental Science, DongNam Health College, 937, Jungja-dong Jangan-gu Suwon 440-714, Korea

[1)]Department of Environmental Engineering, National Hankyong University 67, Sukjung-dong Ansung Kyounggi do 456-749, Korea

(Received 7 February 2006, accepted 29 May 2006)

Abstract

The decomposition of gaseous CH_3CHO was investigated by metal loaded TiO_2 (pure TiO_2, Pt/TiO_2, Pd/TiO_2, Mn/TiO_2 and Ag/TiO_2) with UV/TiO_2 process and $UV/TiO_2/O_3$ process at room temperature and atmospheric pressure. Metal loaded TiO_2 was prepared by photodeposition. Decomposition of CH_3CHO was carried out in a flow-type photochemical reaction system using three 10 W black light lamps (300~400 nm) as a light source. The experimental results showed that the degradation rate of CH_3CHO was increased with Pt and Ag on TiO_2 compared to pure TiO_2, but decreased with depositing Pd and Mn on pure TiO_2. The considerable increase in the degradation efficiency of the CH_3CHO was found by a combination of photocatalysis and ozonation as compared to only by ozonation or photocatalysis. Loading of Pt on TiO_2 promoted conversion of gaseous ozone. The degradation rate of gaseous CH_3CHO decreased with an increase of water vapor in the feed stream for the both UV/TiO_2 and $UV/TiO_2/O_3$ processes. The pure TiO_2 was more affected by the water vapor than Pt loaded TiO_2.

Key words : CH_3CHO, Photodeposition, Pt/TiO_2, Pd/TiO_2, Photocatalysis, Ozonation

1. INTRODUCTION

Indoor air pollution is a serious problem especially in urban area. In recent years, the pollution of volatile organic compounds (VOCs) in indoor air has been increasingly concerned in Korea. Many VOCs can cause headaches, eye, nose, and throat irritation, and dizziness. Some of them are known human carcingens.

In this work, acetaldehyde (CH_3CHO) was used as a model pollutant since it is a contaminant in indoor air (Mark *et al.*, 1996). The CH_3CHO at low concentration was oxidized on TiO_2 and Pt/TiO_2 as a function of temperature. The CH_3CHO might be expected to behave differently from many organics because it desorbs slowly from TiO_2; instead, it reacts to form stable surface species when TiO_2 is heated (Falconer and Magrini-Bair, 1998). The photocatalytic oxidation of CH_3CHO using UV/TiO_2 has been applied to purification of air (Sano *et al.*, 2003; Falconer and Magrini-Bair, 1998; Matsubara *et al.*, 1995; Negishi *et al.*, 1995; Sopyan *et al.*, 1994). Falconer and Magrini-Bair (1998) investi-

* Corresponding author. Tel : +82-31-249-6474,
Fax : +82-31-249-6470, E-mail : ckc@dongnam.ac.kr

gated photocatlytic and thermal catalytic oxidation of CH_3CHO on Pt/TiO_2. Sano *et al.* (2003) reported that in the humid condition, the CH_3CHO degradation rate of Pt/TiO_2 was higher than that of pure TiO_2, however, the degradation rate of Pd or Ag/TiO_2 was lower. The CH_3CHO degradation was partially inhibited by water vapor. The competitive adsorption of CH_3CHO and water molecule seems to decrease the degradation rate. Sopyan *et al.* (1994) reported that at low concentration, photocatalytic oxidation on TiO_2 was first order in CH_3 CHO. At high concentrations and low light intensity, mostly acetic acid formed, but at low concentrations, CO_2 was the primary product.

Ozone should be a potential oxidant for photocatalytic oxidation processes. Some researchers studied the decomposition of VOCs using the UV/TiO_2 process in the presence of ozone. Kopf *et al.* (2000) investigated TiO_2 photocatalytic oxidation of monochloroacetic acid and pyridine: influence of ozone. Zhang and Liu (2004) studied the degradations of trace hexane in the gas phase by O_3/UV, TiO_2/UV and O_3/TiO_2/UV. The degradations of trace toluene in the gas phase by O_3/UV, TiO_2/UV and O_3/TiO_2/UV were studied by Zhang *et al.* (2003). Shen and Ku (2002) investigated the decomposition of gas phase trichloroethene by the UV/TiO_2 process in the presence of ozone. Klare *et al.* (1999) investigated the combination of TiO_2-assisted photocatalysis and ozonation in the degradation of nitrogen containing substrates such as alkylamines, alkanolamines, heterocyclic and aromatic N-compounds.

But there was no report on the photocatalytic decomposition of CH_3CHO by the combined photocatalysis with UV irradiation and ozonation ($UV/TiO_2/O_3$) and by the serveral metal loaded TiO_2 (Pt/TiO_2, Pd/TiO_2, Mn/TiO_2, Ag/TiO_2). This study investigated the degradation of CH_3CHO by four different combinations of ozonation (O_3), photocatalytic treatment with TiO_2 and UV irradiation (UV/TiO_2), combined ozonation and UV irradiation (O_3/UV) and combined photocatalysis with UV irradiation and ozonation ($UV/TiO_2/O_3$) with several metal loded TiO_2 (Pt/TiO_2, Pd/TiO_2, Mn/TiO_2, Ag/TiO_2). The combined photocatalysis and ozonation ($UV/TiO_2/O_3$) is expected to decompose CH_3CHO under such conditions as at room temperature under the presence of water vapor.

2. EXPERIMENTAL

2.1 Preparation of photocatalysts

The supporting material employed to prepare metal doped photocatalysts in this present study was TiO_2 (P25; 80% anatase, crystallite size of 25 nm, specific surface area of 50 $m^2\ g^{-1}$, Nippon Aerosil Ltd.). Metal doped TiO_2 was prepared by photodeposition as follows. The treated TiO_2 powder and aqueous H_2PtCl_6-$6H_2O$ (Pt/TiO_2), $PdCl_2 2NaCl_3$ H_2O (Pd/TiO_2), Mn $(CH_3COO)_2 4H_2O$ (Mn/TiO_2) and $AgNO_3$ (Ag/TiO_2) were added into 80 mL of distilled water in a pyrex vessel with vigorous stirring. The pH of the suspension was adjusted to 6.8 ~ 7.0 by addition of 0.1 N KOH solution with vigorous stirring by a magnetic stirrer. The suspension was bubbled by using high purity nitrogen in order to remove the dissolved O_2, and irradiated with UV light (Ushio, USH-500D, 500 W, high pressure Hg lamp) for 30 min. After the irradiation, the solution containing metal doped TiO_2 catalysts were centrifuged, washed with distilled water until no Cl^- was detected in rinsing water, and dried overnight at about 383 K. The contents of metal doped on TiO_2 were 1.0 wt %.

2.2 Decomposition of actealdehyde

Decomposition of CH_3CHO was carried out in a flow-type photochemical reaction system (50 mm width, 300 mm in length and 5 mm in height) using three 10 W black light lamps (300 ~ 400 nm, FL10NBL, Toshiba Ltd.) as a light source. The catalysts were coated onto the surface of a glass plate (50 mm width and 100 mm in length, 1 mg cm^{-2} of catalyst loading density) using recipe of slurry and dried overnight at 383 K. The air containing CH_3CHO in a concentration of 20 ppm was continuously supplied to the flow type reactor at a constant flow rate 1.0 L min^{-1} throughout this study. When the

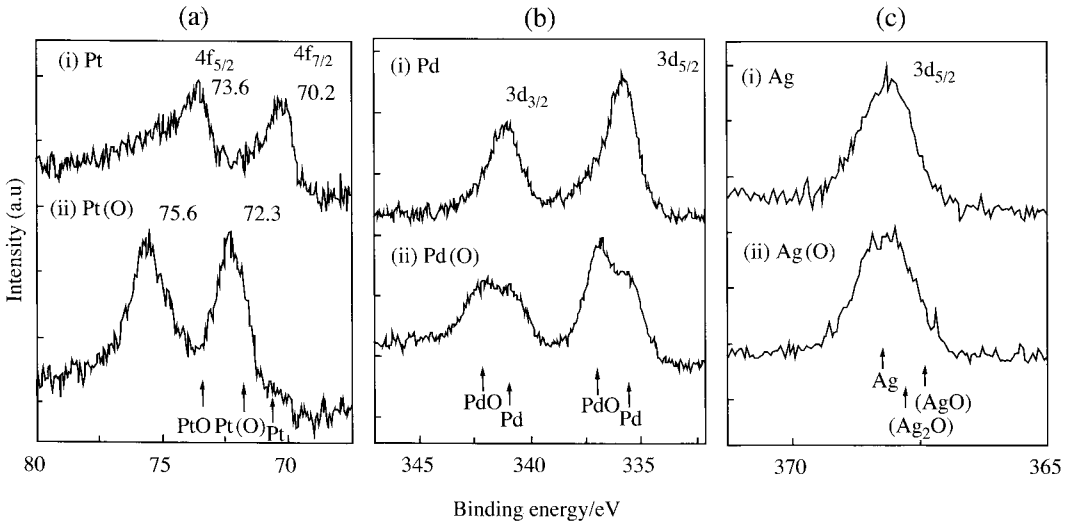

Fig. 1. X-Ray photoelectron spectra of metals photodeposited on TiO_2.

same concentration of CH_3CHO was released with the inlet, UV lamps were turned on. The relative humidity was controlled from 0 to 80% by bubbling the deionized water at a glass saturator. The injected gaseous O_3 concentration in the air stream was varied from 0 to 0.4 micromol min^{-1} to investigate the effect of O_3 added.

A GC (Simadzu GC-14 B) equipped with a FID detector and a column (Zebron ZB-Wax) was used to measure inlet and outlet concentrations of CH_3CHO. The O_3 concentration at the inlet and outlet of the reactor was determined by ozone analyzer with internal and external zero and span (ML 9811, Monitor Labs, Inc.). The CH_3CHO and O_3 concentrations were continuously monitored every 15 min and 30 s with an on-line system, respectively.

3. RESULTS AND DISCUSSION

In the blank tests, the conversion of CH_3CHO by O_3, UV irradiation alone or combined with UV/O_3 was found to be able to ignore under the experimental condition studied in this work. Thus, the effect of UV, O_3 and O_3/UV could be ignored in this study.

3.1 Effects of metal deposition on Photocatalytic decomposition of CH_3CHO in the UV/TiO_2 process

3.1.1 Chemical and electronic structure of metal deposited on TiO_2

The chemical and electronic structure of deposited metals was analyzed by X-ray photoelectron spectra. Fig. 1 shows the typical XPS spectra of the Pt 4f doublet (Pt $4f_{5/2}$ and Pt $4f_{7/2}$), Pd 3d doublet (Pd $3d_{3/2}$ and Pd $3d_{5/2}$) and Ag $3d_{5/2}$. As shown in Fig. 1(a), a large part of Pt was deposited on TiO_2 as metal Pt by photodeposition with methanol, and Pt combined with oxygen was formed mainly without methanol. The binding energy of around 70.2 and 73.6 eV were observed as Pt $4f_{7/2}$ and Pt $4f_{5/2}$ electrons of the Pt metal, respectively. It indicates that Pt photodeposited on TiO_2 surface is a metallic state (Sasaki *et al.*, 2001; Ohtani *et al.*, 1997; Davidson *et al.*, 1987), of which Pt^0 deposited on the catalyst surface functioned not only as the electron trap center but also as the absorption center of O_2 in the photocatalysis (Sclafani and Herrmann, 1998; Chen and White, 1983, 1982). For the Pd photodeposition with methanol, the main peak of Pd $3d_{5/2}$ located at 335.5 eV and a weak shoulder was observed at 336.9 eV (Fig. 1). The main peak was due to metal

Pd and the shoulder was due to PdO. When the photodeposition was performed without methanol, Pd was deposited mostly in the phase of PdO and the minor part was metal Pd. The peak center of Ag $3d_{5/2}$ located at 368.2 eV when Ag species were photodeposited on TiO_2 with methanol (Fig. 1). In the spectrum of the photocatalyst prepared without methanol, the minor component due to Ag_2O (367.8 eV) or AgO (367.4 eV) was observed. The photocatalysts with Pd and Ag prepared without methanol will be represented as Pd (O)-TiO_2 and Ag (O)-TiO_2.

3.1.2 The decomposition of CH_3CHO in the UV/TiO_2 process

Effects of metal-photodeposited platinum (Pure TiO_2, Pt/TiO_2, Pd/TiO_2, Mn/TiO_2 and Ag/TiO_2) on photocatalytic decomposition of CH_3CHO by UV/TiO_2 process were shown in Fig. 2. It was found that the degradation rate of CH_3CHO was increased with depositing Pt and Ag on TiO_2 compared to pure TiO_2, but decreased with depositing Pd and Mn on pure TiO_2. This suggests that the metal Pt and Ag phase have higher activity as a co-catalyst for CH_3CHO degradation with TiO_2. Pt and Ag may increase the O_2 concentration on the pure TiO_2 surface and thus accelerate photocatalytic oxidation. The increase in photocatalytic decomposition activity with the depositing of Pt on Pure TiO_2 has been explained by electron trapping in the Pt particles and this was proposed to lower e^-/h^+ recombination rates (Wang *et al.*, 1992; Schindler and Kunst, 1990; Gersicher, 1984; Disidier *et al.*, 1983). Falconer and Magrini-Bair (1998) reported that Pt supplies spillover oxygen onto the TiO_2 which further oxidizes the acetaldehyde decomposition products. Therefore deactivation is dramatically slowed and oxidation of the acetaldehyde occurs efficiently. Imamura *et al.* (1991) reported, in the decomposition of O_3 on a silver catalyst, that the activity of the metal oxide catalysts increased roughly in the order of the increase in their surface area and in the amount of surface oxygen on them.

It was found that the degradation rate of acetaldehyde was decreased with deposition of Pd or Mn

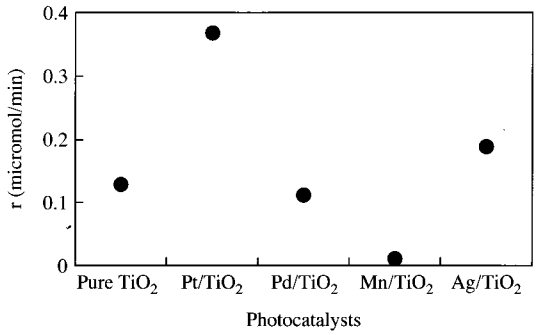

Fig. 2. Effect of photodeposited metal species on the reaction rate of acetaldehyde by UV/TiO_2 process. (flow rate: 1.0 L/min, UV intensity: 0.49 mW/cm^2 at 300~400 nm, Co: 20~21 ppm, RH: 0%).

compared to pure TiO_2. The inhibiting effect of halogenated compounds on the catalytic activity of supported Pd and Pt catalysts with respect to the total oxidation of methane was first reported by Cullis and Willatt (1984). Pd catalysts appeared more sensitive to poisoning than Pt ones. But, no clear explanation for the decrease of the catalytic activity was given. Supported Pd and Pt catalysts are usually prepared by impregnation of the support with Cl^- containing metal precursors. It turns out that conventional activation treatments do not allow the complete removal of chloride ions originating from the metal precursor. Therefore, a possible explanation may be that residual chlorine originating from Cl^- containing the Pd precursor is responsible for an inhibition in the degradation of acetaldehyde in this study.

In case of Mn-photodeposited platinum (Mn/TiO_2), there is no removal efficiency of acetaldehyde.

3.2 Photocatalytic ozonation of acetaldehyde in the UV/TiO_2/O_3 process

The photocatalytic ozonation is a photoreaction which needs all the three components: titanium dioxide, ozone and UV light. Probably the direct ozone oxidation of the acetaldehyde also happens during illumination. But a further contribution to the degradation of the acetaldehyde should be initiated

by the reaction of the ozone with the illuminated titanium dioxide (Kopt *et al.*, 2000).

3.2.1 Effect of O_3 concentration injected on decomposition of acetaldehyde

Fig. 3 indicates the ozone dosage effect on the decomposition of gaseous acetaldehyde by UV/TiO_2/O_3 process with pure TiO_2, Pt/TiO_2, Pd/TiO_2, Mn/TiO_2 and Ag/TiO_2, respectively. It was found that the addition of ozone can improve the decomposition of acetaldehyde in all metal deposited TiO_2 in this work. From the experimental results obtained, it is obvious that there exists a synergic effect between TiO_2, O_3 and UV light (Klare *et al.*, 1999). In case of Pt/TiO_2, however, excessive ozone would reduce the decomposition efficiency of acetaldehyde by the UV/TiO_2/O_3 process, because of excess ozone molecules scavenging hydroxyl radicals produced from the excitation of TiO_2 by UV radiation. On the other hand, the enhanced degradation efficiency can be attributed to the formation of hydrophilic intermediate compounds by O_3, so that the attack of electrophilic hydroxyl radicals more quickly leads to carbon dioxide. This effect is well-known from photocatalysis with ozonation.

In fact, besides direct ozonation of the intermediate compounds Zhang *et al.* (2003) reported that in the presence of illuminated TiO_2, O_3 can generate hydroxyl radicals by the formation of an ozonide radical ($O_3^{\bullet -}$) in the adsorption layer (Eq. 1-4). The hydroxyl radical is considered to be the reactive species for the breakdown of organic compounds. The generation of hydroxyl radical can be generally described as follows:

$$TiO_2 + hv \rightarrow e^- + h^+ \quad (1)$$

$$O_3 + e^- \rightarrow O_3^{\bullet -} \quad (2)$$

$$H^+ + O_3^{\bullet -} \rightarrow HO_3^{\bullet} \quad (3)$$

$$HO_3^{\bullet} \rightarrow O_2 + OH^{\bullet} \quad (4)$$

The effect of ozone dosage on the relative decomposition rate of acetaldehyde by combined photocatalytic ozonation (UV/TiO_2/O_3 process) was shown in Fig. 3(b). In the case of Mn/TiO_2, it was found that the decomposition rate of acetaldehyde was

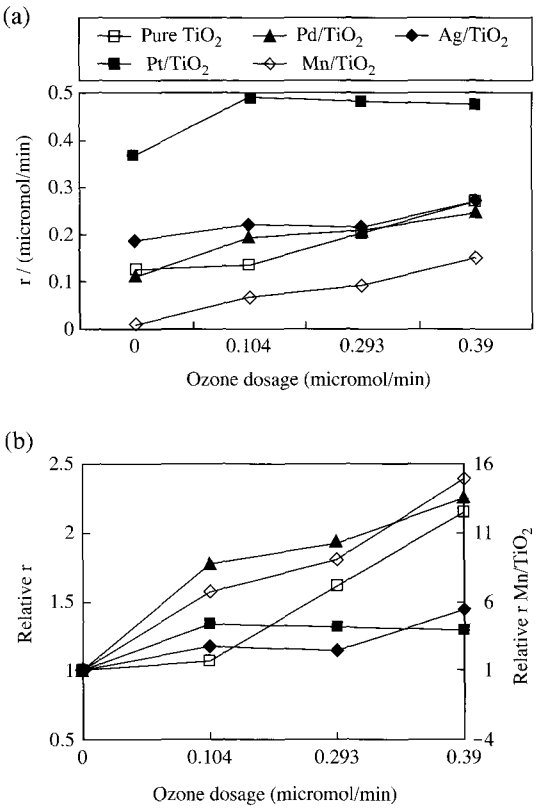

Fig. 3. Effect of ozone dosage concentration on the reaction rate (a) and relavtive reaction rate (b) of acetaldehyde by combined photocatalytic ozonation (UV/TiO_2/O_3 process). (flow rate: 1.0 L/min, UV intensity: 0.49 mW/cm^2 at 300 ~ 400 nm, RH: 0%).

lower than that in other metal-deposited TiO_2 when ozone was not added (Fig. 3(a)), but the effect of ozone concentration were much more significant in photocatlytic ozonation process. The slope was nearly 16 times of that in the later.

Generally, when ozone is added on reaction, decomposition rate of acetaldehyde appears higher than when it is not added in this work.

By resulting in this study to effect on the decomposition of gaseous acetaldehyde with various metal-loaded TiO_2, it was found that the degradation rate of gaseous acetaldehyde was the highest in the photodeposited platinum (Pt/TiO_2). Fig. 4 shows ozone conversion with pure TiO_2 and Pt/TiO_2 by UV/TiO_2/O_3 process. As shown in Fig. 4 the conver-

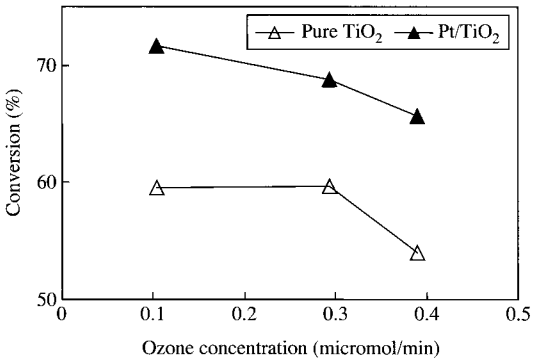

Fig. 4. Comparision of ozone conversion by $UV/TiO_2/O_3$ process.

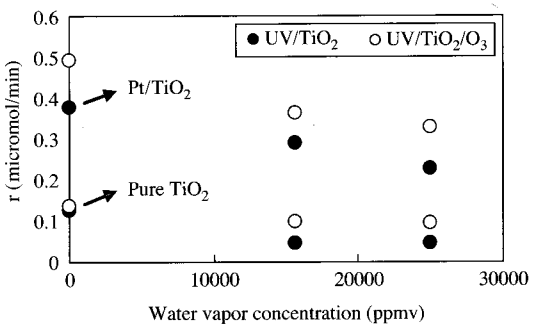

Fig. 5. Effect of water vapor concentration on reaction rate of acetaldehyde by UV/TiO_2 and $UV/TiO_2/O_3$ process. (flow rate: 1.0 L/min, UV intensity: 0.49 mW/cm² at 300~400 nm, RH: 0%, $[O_3]_0$: 0.10 μmol/L).

sion of ozone promoted by the loading of Pt on TiO_2. Pt may increase the O_2 concentration on the TiO_2 surface and thus accelerate photocatalytic oxidation.

3.2.2 Effect of water vapor

Fig. 5 shows effect of water vapor concentration on reaction rate of acetaldehyde by UV/TiO_2 and $UV/TiO_2/O_3$ process. As previously reported (Zhao and Yang, 2003; Gregory and Craig, 1993), the presence of water vapor competes with pollutants for adsorption sites on TiO_2 thus reducing the pollutant removal rate. High humidity in the feed stream significantly inhibited the oxidation rate of acetaldehyde since water was preferentially adsorbed on the hydrophilic surface of TiO_2. In this study, different volume percentages of water vapor were added to a fixed CH_3CHO concentration level of 20 ppmv in order to examine the effect of water vapor on the photocatalytic decomposition and photocatalytic ozonation of gaseous CH_3CHO. It was found that the pure TiO_2 was more affected by the water vapor than Pt loaded TiO_2 since deactivation was much slower on Pt/TiO_2 than on TiO_2. Fu *et al.* (1995) also reported differences in accumulation on the surface for photocatalytic oxidation of benzene on TiO_2 and 0.1% Pt/TiO_2. They observed a yellow color on TiO_2 after reaction but no color change for Pt/TiO_2. Thus, even a low loading of Pt may be sufficient to slow deactivation significantly. In this study, both of them (pure TiO_2 and Pt/TiO_2) showed a decreased in the conversion of CH_3CHO with increasing water vapor in the feed stream. Anpo *et al.* (1994) have claimed that the addition of water onto oxides causes structural changes in surface band bending, which enhances the efficiency of electron-hole recombination, and thus reduces photocatalytic reaction rate. It was also found that in this study the decomposition rate of CH_3CHO was higher with $UV/TiO_2/O_3$ process than with UV/TiO_2 process.

4. CONCLUSIONS

In this study, we investigated and compared decomposition of gaseous CH_3CHO by metal loaded TiO_2 (pure TiO_2, Pt/TiO_2, Pd/TiO_2, Mn/TiO_2 and Ag/TiO_2) with UV/TiO_2 process and $UV/TiO_2/O_3$ process. The degradation rate of CH_3CHO was high with Pt or Ag deposition comparing to pure TiO_2 in the UV/TiO_2 process. It means that facilitate to decompose CH_3CHO in the photocatalytic process. However, Pd and Mn did not show any effect on decomposition of acetaldehyde. The photocatalytic ozonation of CH_3CHO can improve the decomposition of CH_3CHO in all metal-loaded TiO_2 in the $UV/TiO_2/O_3$ process. The degradation rate of CH_3CHO increased with an increase in ozone dosage in the reaction. In case of Pt/TiO_2, however,

excessive ozone would reduce the degradation rate of CH_3CHO by the $UV/TiO_2/O_3$ process since ozone molecules could scavenge hydroxyl radicals produced from the excitation of TiO_2 by UV radiation to inhibit the decomposition of CH_3CHO. It was found that the conversion of gaseous ozone promoted by the loading of Pt on TiO_2. The degradation rate of gaseous CH_3CHO decreased with an increase of water vapor in the feed stream for the both UV/TiO_2 and $UV/TiO_2/O_3$ processes. It was also found that the decomposition rate of CH_3CHO was higher with $UV/TiO_2/O_3$ process than with UV/TiO_2 process.

Thus, the combination of photocatalysis and photocatalytic ozonation could be an alternative process to decompose for gaseous CH_3CHO under specific conditions.

ACKNOWLEDGEMENT

This work was supported by the funded (2006) from DongNam Health College.

REFERENCES

Anpo, M., K. chiba, M. Tomonari, S. Coluccia, M. Che, and M.A. Fox (1994) Bull. Chem. Soc. Jpn. 64, 543.

Chen, B.H. and J.M. White (1982) Properties of platinum supported on oxides of titanium J. Phys. Chem. 86(18), 3534-3541.

Chen, B.H. and J.M. White (1983) Behavior of titanium (3+) centers in the low-temperature reduction of platinum/titania/potassium systems J. Phys. Chem. 87(8) 1327-1329.

Cullis, C.F. and B.M. Willatt (1984) The inhibition of hydrocarbon oxidation over supported precious metal catalysts. J. Catal. 86, 187-200.

Davidson, M.R., G.B. Hoflund, L. Niinisto, and H.A. Laitinen (1987) Electrochemisorption of hexahydroxylplatinate (IV) on thin titania films. J. Electroanal. Chem. 228, 471-480.

Disidier, J., J.M. Herrmann, and P. Pichat (1983) A Photoconductivity study of electron transfer from the ultraviolet-illuminated support to the metal and of the influence of hydrogen. J. Chem. Soc. Faraday Trans. I 79, 651-660.

Falconer, J.L. and K.A. Magrini-Bair (1998) Photocatalytic and thermal catalytic oxidation of acetaldehyde on Pt/TiO_2. J. Catal. 179, 171-178.

Fu, X., W.A. Zeltner, and M.A. Anderson (1995) The gas-phase photocatalytic mineralization of benzene on porous titania-based catalysts. Appl. Catal. B 6, 209-224.

Gersicher, H. (1984) A mechanism of electron hole pair separation in illuminated semiconductor particles J. Phys. Chem. 88(25), 6096-6097.

Gregory B.R. and T.J. Craig (1993) Photocatalytic oxidation of oxygenated air toxics. Applied Surface Science 72, 321-327.

Imamura, S., M. Ikebata, T. Ito, and T. Ogita (1991) Decomposition of ozone on a silver catalyst. Ind. Eng. Chem. Res. 30, 217-221.

Klare, M., G. Waldner, R. Bauer, H. Jacobs, and J.A.C. Broekaert (1999) Degradation of nitrogen containing organic compounds by combined photocatalysis and ozonation. Chemosphere, 38(9), 2013-2027.

Kopf, P., E. Gilbert, and S.H. Eberle (2000) TiO_2 photocatalytic oxidation of monochloroacetic acid and pyridine: influence of ozone. J. Photochem. Photobiol. A 136, 163-168.

Mark, R.N., J.W. Edward, L.B. Matthew, A.F. John, and B. Gayle (1996) Gas-phase heterogeneous photocatalytic oxidation of ethanol: pathways and kinetic modeling. Environ. Sci. Technol. 30, 3102-3110.

Matsubara, H., M. Takada, S. Koyama, K. Hashimoto, and A. Fujishima (1995) Photoactive TiO_2 containing paper. Preparation and its photocatalytic activity under weak UV light illumination. Chem. Lett. 767-768.

Negishi, N., T. Iyoda, K. Hashimoto, and A. Fujishima (1995) Preparation of tansparent TiO_2 thin film photocatalyst and its photocatalytic activity. Chem. Lett., 841-842.

Ohtani, B., K. Iwai, S. Nishimoto, and S. Sato (1997) Role of platinum deposits on titanium (IV) oxide particles: Structural and kinetic analyses of photocatalytic reaction in aqueous alcohol and amino acid solutions. J. Phys. Chem. B 101(17), 3349-3359.

Sano, T., N. Negishi, K. Uchino, J. Tanaka, S. Matsuzawa,

and K. Takeuchi (2003) Photocatalytic degradation of gaseous acetaldehyde on TiO_2 with photodeposited metals and metal oxides. J. Photochem. Photobiol. A 160, 93-98.

Sasaki, T., N. Koshizaki, J.W. Yoon, and K.M. Beck (2001) Preparation of Pt/TiO_2 nanocomposite thin films by pulsed laser deposition and their photoelectrochemical behaviors. J. Photochem. Photobiol. A 145, 11-16.

Schindler, K.M. and M. Kunst (1990) Charge-carrier dynamics in titania powders J. Phys. Chem. 94(21), 8222-8226.

Sclafani, A. and J.M. Herrmann (1998) Influence of metallic silver and of platinum-silver bimetallic deposits on the photocatalytic activity of titania (anatase and rutile) in organic and aqueous media. J. Photochem. Photobiol. A 113, 181-188.

Shen, Y.S. and Y. Ku (2002) Decomposition of gas-phase trichloroethene by the UV/TiO_2 process in the presence of ozone. Chemosphere 46, 101-107.

Sopyan, I., S. Murasawa, K. Hahimoto, and A. Fujishima (1994) Highly efficient TiO_2 film photcatalyst. Degradation of gaseous acetaldehyde. Chem. Lett. 723-726.

Wang, C.M., A. Heller, and H. Gerischer (1992) Palladium catalysis of O_2 reduction by electrons accumulated on TiO_2 particles during photoassisted oxidation of organic compounds. J. Am. Chem. Soc. 114(13), 5230-5234.

Zhang, P., L. Fuyan, Y. Gang, C. Qing, and Z. Wanpeng (2003) A comparative study on decomposition of gaseous toluene by O_3/UV, TiO_2/UV and O_3/TiO_2/UV. J. Photochem. Photobiol. A 156, 189-194.

Zhang, P. and J. Liu (2004) Photocatalytic degradation of trace hexane in the gas phase with and without ozone addition: kinetic study. J. Photochem. Photobiol. A 167, 87-94.

Zhao, J. and X. Yang (2003) Photocatalytic oxidation for indoor air purification: a literature review. Building and Environment 38, 645-654.