Photocatalytic Decomposition of Gaseous Acetaldehyde by Metal Loaded TiO₂ with Ozonation

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Abstract

The decomposition of gaseous CH₃CHO was investigated by metal loaded TiO₂ (pure TiO₂, Pt/TiO₂, Pd/TiO₂, Mn/TiO₂ and Ag/TiO₂) with UV/TiO₂ process and UV/TiO₂/O₂ process at room temperature and atmospheric pressure. Metal loaded TiO₂ was prepared by photodeposition. Decomposition of CH₃CHO 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 CH₃CHO was increased with Pt and Ag on TiO₂ compared to pure TiO₂, but decreased with depositing Pd and Mn on pure TiO₂. The considerable increase in the degradation efficiency of the CH₃CHO was found by a combination of photocatalysis and ozonation as compared to only by ozonation or photocatalysis. Loading of Pt on TiO₂ promoted conversion of gaseous ozone. The degradation rate of gaseous CH₃CHO decreased with an increase of water vapor in the feed stream for the both UV/TiO₂ and UV/TiO₂/O₂ processes. The pure TiO₂ was more affected by the water vapor than Pt loaded TiO₂.

Key words: CH₃CHO, Photodeposition, Pt/TiO₂, Pd/TiO₂, 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 carcinogens.

In this work, acetaldehyde (CH₃CHO) was used as a model pollutant since it is a contaminant in indoor air (Mark et al., 1996). The CH₃CHO at low concentration was oxidized on TiO₂ and Pt/TiO₂ as a function of temperature. The CH₃CHO might be expected to behave differently from many organics because it desorbs slowly from TiO₂; instead, it reacts to form stable surface species when TiO₂ is heated (Falconer and Magrini-Bair, 1998). The photocatalytic oxidation of CH₃CHO using UV/TiO₂ has been applied to purification of air (Sano et al., 2003; Falconer and Magrini-Bair, 1998; Matusbara et al., 1995; Negishi et al., 1995; Sopyan et al., 1994). Falconer and Magrini-Bair (1998) investi-
gated photocatalytic and thermal catalytic oxidation of CH$_3$CHO on Pt/TiO$_2$. Sano et al. (2003) reported that in the humid condition, the CH$_3$CHO 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$_3$CHO degradation was partially inhibited by water vapor. The competitive adsorption of CH$_3$CHO 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.


But there was no report on the photocatalytic decomposition of CH$_3$CHO 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$_3$CHO 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 loaded 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 decom pose CH$_3$CHO 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 photo-deposition as follows. The treated TiO$_2$ powder and aqueous H$_2$PtCl$_6$·6H$_2$O (Pt/TiO$_2$), PdCl$_2$2NaCl$_3$ H$_2$O (Pd/TiO$_2$), Mn (CH$_3$COO)$_2$4H$_2$O (Mn/TiO$_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 acetaldehyde

Decomposition of CH$_3$CHO 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$_3$CHO 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
same concentration of CH₂CHO 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 O₃ concentration in the air stream was varied from 0 to 0.4 micromol min⁻¹ to investigate the effect of O₃ added.

A GC (Shimadzu GC-14 B) equipped with a FID detector and a column (Zebron ZB-Wax) was used to measure inlet and outlet concentrations of CH₃CHO. The O₃ 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 CH₂CHO and O₃ 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 CH₂CHO by O₃, UV irradiation alone or combined with UV/O₃ was found to be able to ignore under the experimental condition studied in this work. Thus, the effect of UV, O₃ and O₃/UV could be ignored in this study.

3.1 Effects of metal deposition on Photocatalytic decomposition of CH₂CHO in the UV/TiO₂ process

3.1.1 Chemical and electronic structure of metal deposited on TiO₂

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 4f₁/₂ and Pt 4f₃/₂), Pd 3d doublet (Pd 3d₅/₂ and Pd 3d₃/₂) and Ag 3d₅/₂. As shown in Fig. 1(a), a large part of Pt was deposited on TiO₂ 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 4f₃/₂ and Pt 4f₁/₂ electrons of the Pt metal, respectively. It indicates that Pt photodeposited on TiO₂ surface is a metallic state (Sasaki et al., 2001; Ohtani et al., 1997; Davidson et al., 1987), of which Pt⁰ deposited on the catalyst surface functioned not only as the electron trap center but also as the absorption center of O₂ in the photocatalysis (Scafani and Herrmann, 1998; Chen and White, 1983, 1982). For the Pd photodeposition with methanol, the main peak of Pd 3d₅/₂ 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 TiO₂ with methanol (Fig. 1). In the spectrum of the photocatalyst prepared without methanol, the minor component due to Ag₂O (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)-TiO₂ and Ag (O)-TiO₂.

3.1.2 The decomposition of CH₃CHO in the UV/TiO₂ process

Effects of metal-photodeposited platinum (Pure TiO₂, Pt/TiO₂, Pd/TiO₂, Mn/TiO₂ and Ag/TiO₂) on photocatalytic decomposition of CH₃CHO by UV/TiO₂ process were shown in Fig. 2. It was found that the degradation rate of CH₃CHO was increased with depositing Pt and Ag on TiO₂ compared to pure TiO₂, but decreased with depositing Pd and Mn on pure TiO₂. This suggests that the metal Pt and Ag phase have higher activity as a co-catalyst for CH₃CHO degradation with TiO₂. Pt and Ag may increase the O₂ concentration on the pure TiO₂ surface and thus accelerate photocatalytic oxidation. The increase in photocatalytic decomposition activity with the depositing of Pt on Pure TiO₂ 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; Gerscher, 1984; Disidier et al., 1983). Falconer and Magrini-Bair (1998) reported that Pt supplies spillover oxygen onto the TiO₂ 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 O₃ 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 compared to pure TiO₂. 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/TiO₂), there is no removal efficiency of acetaldehyde.

3.2 Photocatalytic ozonation of acetaldehyde in the UV/TiO₂/O₃ 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\textsubscript{3} concentration injected on decomposition of acetaldehyde

Fig. 3 indicates the ozone dosage effect on the decomposition of gaseous acetaldehyde by UV/TiO\textsubscript{2}/O\textsubscript{3} process with pure TiO\textsubscript{2}, Pt/TiO\textsubscript{2}, Pd/TiO\textsubscript{2}, Mn/TiO\textsubscript{2} and Ag/TiO\textsubscript{2}, respectively. It was found that the addition of ozone can improve the decomposition of acetaldehyde in all metal deposited TiO\textsubscript{2} in this work. From the experimental results obtained, it is obvious that there exists a synergic effect between TiO\textsubscript{2}, O\textsubscript{3} and UV light (Klare et al., 1999). In case of Pt/TiO\textsubscript{2}, however, excessive ozone would reduce the decomposition efficiency of acetaldehyde by the UV/TiO\textsubscript{2}/O\textsubscript{3} process, because of excess ozone molecules scavenging hydroxyl radicals produced from the excitation of TiO\textsubscript{2} by UV radiation. On the other hand, the enhanced degradation efficiency can be attributed to the formation of hydrophilic intermediate compounds by O\textsubscript{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\textsubscript{2}, O\textsubscript{3} can generate hydroxyl radicals by the formation of an ozonide radical (O\textsubscript{3}\(^{\cdot-}\)) 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:

\[ TiO_2 + h\nu \rightarrow e^- + h^+ \]  \hspace{1cm} (1)

\[ O_3 + e^- \rightarrow O_3^{\cdot-} \]  \hspace{1cm} (2)

\[ H^+ + O_3^{\cdot-} \rightarrow HO_3^{\cdot} \]  \hspace{1cm} (3)

\[ HO_3^{\cdot} \rightarrow O_2 + OH^{\cdot} \]  \hspace{1cm} (4)

The effect of ozone dosage on the relative decomposition rate of acetaldehyde by combined photocatalytic ozonation (UV/TiO\textsubscript{2}/O\textsubscript{3} process) was shown in Fig. 3(b). In the case of Mn/TiO\textsubscript{2}, it was found that the decomposition rate of acetaldehyde was lower than that in other metal-deposited TiO\textsubscript{2} when ozone was not added (Fig. 3(a)), but the effect of ozone concentration were much more significant in photocatalytic 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\textsubscript{2}, it was found that the degradation rate of gaseous acetaldehyde was the highest in the photodeposited platinum (Pt/TiO\textsubscript{2}). Fig. 4 shows ozone conversion with pure TiO\textsubscript{2} and Pt/TiO\textsubscript{2} by UV/TiO\textsubscript{2}/O\textsubscript{3} process. As shown in Fig. 4 the conver-
sion of ozone promoted by the loading of Pt on TiO₂. Pt may increase the O₂ concentration on the TiO₂ 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/TiO₂ and UV/TiO₂/O₃ process. As previously reported (Zhao and Yang, 2003; Gregory and Craig, 1993), the presence of water vapor competes with pollutants for adsorption sites on TiO₂ 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 TiO₂. In this study, different volume percentages of water vapor were added to a fixed CH₃CHO concentration level of 20 ppmv in order to examine the effect of water vapor on the photocatalytic decomposition and photocatalytic ozonation of gaseous CH₃CHO. It was found that the pure TiO₂ was more affected by the water vapor than Pt loaded TiO₂ since deactivation was much slower on Pt/TiO₂ than on TiO₂. Fu et al. (1995) also reported differences in accumulation on the surface for photocatalytic oxidation of benzene on TiO₂ and 0.1% Pt/TiO₂. They observed a yellow color on TiO₂ after reaction but no color change for Pt/TiO₂. Thus, even a low loading of Pt may be sufficient to slow deactivation significantly. In this study, both of them (pure TiO₂ and Pt/TiO₂) showed a decreased in the conversion of CH₃CHO 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 CH₃CHO was higher with UV/TiO₂/O₃ process than with UV/TiO₂ process.

4. CONCLUSIONS

In this study, we investigated and compared decomposition of gaseous CH₃CHO by metal loaded TiO₂ (pure TiO₂, Pt/TiO₂, Pd/TiO₂, Mn/TiO₂ and Ag/TiO₂) with UV/TiO₂ process and UV/TiO₂/O₃ process. The degradation rate of CH₃CHO was high with Pt or Ag deposition comparing to pure TiO₂ in the UV/TiO₂ process. It means that facilitate to decompose CH₃CHO in the photocatalytic process. However, Pd and Mn did not show any effect on decomposition of acetaldehyde. The photocatalytic ozonation of CH₃CHO can improve the decomposition of CH₃CHO in all metal-loaded TiO₂ in the UV/TiO₂/O₃ process. The degradation rate of CH₃CHO increased with an increase in ozone dosage in the reaction. In case of Pt/TiO₂, however,
excessive ozone would reduce the degradation rate of CH$_3$CHO 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$_3$CHO. It was found that the conversion of gaseous ozone promoted by the loading of Pt on TiO$_2$. The degradation rate of gaseous CH$_3$CHO decreased with an increase of water vapor in the feed stream for both UV/TiO$_2$ and UV/TiO$_2$/O$_3$ processes. It was also found that the decomposition rate of CH$_3$CHO 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$_3$CHO under specific conditions.

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