

Photocatalytic degradation of gaseous acetaldehyde on TiO₂ with photodeposited metals and metal oxides

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Abstract

The photocatalytic degradation of acetaldehyde by metal-photodeposited TiO₂ was analyzed at room temperature and elevated temperatures. In the humid condition, the acetaldehyde degradation rate of Pt–TiO₂ was larger than that of pure TiO₂, however, the degradation rate of Pd or Ag–TiO₂ was smaller. The degradation rate of metal-deposited TiO₂ depended on the oxidation state of metal, which also influenced the signal intensities of O₂[−] and Ti³⁺ in electron spin resonance (ESR) spectrum recorded at 77 K. By elevating temperature from 40 to 130 °C, the acetaldehyde degradation rate and the CO₂ production rate of Pt–TiO₂ were increased by the aid of metal Pt. Acetaldehyde is also thermocatalytically degraded by photodeposited Pt on TiO₂ at 70–190 °C without UV irradiation, however the UV irradiation is necessary for complete mineralization of acetaldehyde. The mineralization of acetaldehyde is considered to be enhanced by the partial oxidation of acetaldehyde by Pt thermocatalyst and the oxidation of intermediates into CO₂ by TiO₂ photocatalyst.

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1. Introduction

Photocatalytic degradation of volatile organic compounds (VOCs), such as aldehydes, aromatic compounds and chlorinated ethylenes, using UV-illuminated TiO₂ is proposed as an alternative advanced oxidation process for the purification of water and air [1–4]. In an ideal photocatalytic mineralization of VOCs, they will be oxidized into CO₂ and H₂O (and HCl when the VOC contains chlorine). In the photocatalytic degradation of acetaldehyde by TiO₂, the complete oxidation into CO₂ and H₂O was observed in the batch type reactors [5,6]. On the other hand, the formation of carbonic acid and coke-like substances was observed in the flow type reactor. All of the formed coke-like substances could be thermocatalytically removed as CO₂ by heating the photocatalyst up to 400 °C when the Pt-deposited photocatalyst was used [7]. The acetaldehyde degradation was partially inhibited by water vapor in our preliminary experiment. The competitive adsorption of acetaldehyde and water molecule seems to decrease the degradation rate. Since the polluted air contains water vapor in most cases, the modification of

TiO₂ that increases the activity in humid condition would be important.

The addition of noble metals, such as Pt, Au, and Pd, on TiO₂ may provide two types of enhancement effects on the acetaldehyde degradation; one is for photocatalytic activity attributable to an increase in charge separation efficiency [8], and the other is for thermocatalytic activity attributable to surface of nanoparticle metals. The increase in charge separation efficiency will enhance the formation of active oxygen species, which improves the degradation rate. The thermocatalytic activity may enhance the dark reactions in acetaldehyde degradation, and the active species formed by UV absorption would be efficiently utilized for the light reaction. This scheme will be effective on the increase in total degradation rate at elevated temperatures. However only a few authors have reported the mineralization of VOCs at elevated temperatures [4,9,10]. Anderson et al. reported that the degradation rate of trichloroethylene (TCE) by TiO₂ did not change, but the stoichiometry ratio (moles of CO₂ produced)/(moles of TCE degraded) increased by elevating the temperature from 23 to 62 °C. Avila et al. reported that the photocatalytic TCE degradation by Pt-loaded TiO₂ decreased dramatically above 130 °C, likely due to the low adsorption of TCE on the catalyst surface at higher temperatures. Fu et al. reported that the photocatalytic conversion

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of benzene by pure TiO₂ was slightly enhanced by elevating temperature and the conversion of benzene by Pt–TiO₂ was increased significantly between 90 and 130 °C. The increase in the performance was ascribed to thermocatalytic activity of Pt. From these reports, the effect of temperature on photocatalytic reaction strongly depends on the target molecule and deposited metals.

In the present paper, metal- and metal oxide-loaded TiO₂ photocatalysts were synthesized and the acetaldehyde degradation by the photocatalysts was analyzed under humid condition. The effects of metal deposition, oxidation state of metal species, water vapor and reaction temperature were studied.

2. Experimental

2.1. Preparation of metal-deposited TiO₂

The Pt, Pd, and Ag loaded TiO₂ were prepared by photodeposition method [11,12]. Anatase type TiO₂ (Degussa, P25) was dispersed into H₂PtCl₆·6H₂O, PdCl₂ and AgNO₃ solution (1.25×10^{-4} to 1.88×10^{-3} mol dm⁻³). The pH of the suspension was adjusted to 6.8 by adding KOH solution (0.01 – 0.1 mol dm⁻³) while the suspension was stirred vigorously by a magnetic stirrer. The suspension was poured into a quartz cell for photodeposition and was aged for 30 min at room temperature. Methanol was added to suspension as a reductant (or hole scavenger) to reduce metal species. UV light from a high pressure Hg lamp (Ushio, USH-500D, 500 W) was irradiated to the suspension through a longpass filter (cut-off wavelength, 295 nm) for 30 min while N₂ gas was passed through the suspension (photodeposition process). The product was washed with distilled water four times by the aid of centrifugation. The amount of metal species deposited on TiO₂ were approximately 90% (Pt), 60% (Pd) and 95% (Ag) of the contents of metal ions in the suspension when the metal content in suspension was less than 1 wt.% against TiO₂.

2.2. Degradation of acetaldehyde by metal-deposited TiO₂

The degradation of acetaldehyde was analyzed using the flow type reactor is shown in Fig. 1. The suspension in-

cluding 0.1 g portion of photocatalyst was coated on the inner glass tube (external diameter: 12 mm) and dried at 383 K for 12 h to fix the photocatalyst. The coated area was 100 cm². The glass tube with photocatalyst was placed in another Pyrex glass tube (internal diameter: 25 mm, length 500 mm). The both side of outer tube were sealed by silicone plugs with a gas inlet. The surface of photocatalyst was cleaned by UV irradiation in dry air over 10 h until the CO₂ concentration in the effluent gas was lower than 5 ppm to remove organic impurities. After the purification of the surface of photocatalyst, 100 ppm of acetaldehyde in 50% humid air was introduced into the single pass reactor at the flow rate of 1 dm³/min while UV light was irradiated to the photocatalyst. The UV source was six 10 W black light bulbs (Toshiba FL10BL) surrounding the reactor, and the UV irradiance at the photocatalyst was approximately 0.5 mW/cm². The temperature of photocatalyst was controlled to be 40–190 °C by electric heater placed in the inner tube and a regulator with thermocouples. The effluent gas was analyzed using two gas chromatographs with a thermal conductivity detector (TCD) and a flame ionization detector (FID). A flat type reactor was also used for the analysis of the degradation at room temperature; reactor volume: 450 cm³, coated area: 100 cm², UV irradiance: 0.5 mW/cm².

The solid phases were identified by powder X-ray diffraction (XRD) with Cu K α radiation (Rigaku, model RU-300) and X-ray photoelectron spectroscopy (XPS) with Al K α radiation (Fisons instruments, Escalab220i-XL). The amounts of deposited metals were determined by X-ray fluorescence analysis (XRF; Philips, PW2404). Electron spin resonance (ESR) spectra were recorded at 77 K with a JEOL JES-TE300 ESR spectrometer. A 0.10 g portion of the photocatalyst was placed in a sample tube of Suprasil quartz-glass, and the tube was sealed at atmospheric pressure and room temperature. The *g* value was corrected by a Mn²⁺ marker. The photocatalysts were heat-treated at 110 °C in air for 3 h to eliminate excess adsorbed water and then cooled down in ambient air (humidity 45–55%) before ESR measurement. Since the adsorbed water on TiO₂ is not completely removed from surface at 110 °C [13], the amount of adsorbed water after the treatment is considered to be moderate to discuss the photocatalytic activity in the presence of water vapor.

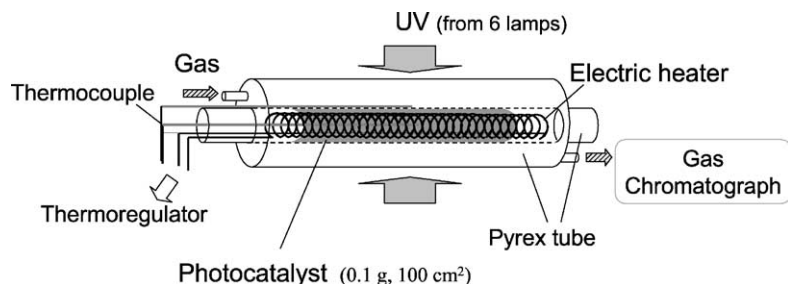


Fig. 1. Experimental setup for photocatalytic degradation of acetaldehyde (AcH) at elevated temperature between 40 and 190 °C.

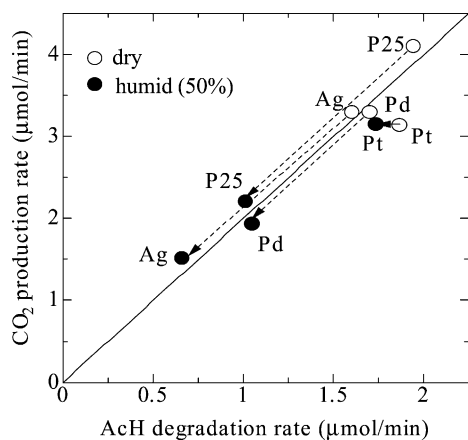


Fig. 2. Photocatalytic activities of metal-deposited TiO₂ on acetaldehyde degradation and CO₂ production. The activities in dry condition are represented by open circles and those in humid condition are represented by filled circle. The loaded amount of Pt, Pd and Ag were 0.2, 0.12 and 0.2 wt.% against TiO₂, respectively.

3. Results and discussion

3.1. Effects of metal deposition on photocatalytic degradation of acetaldehyde

All the metal-photodeposited TiO₂ (Pt–TiO₂, Pd–TiO₂, Ag–TiO₂) degraded acetaldehyde to produce CO₂. Only small amount of methane (3 ppm at maximum), methanol and acetone were detected as gaseous byproduct. Fig. 2 shows the acetaldehyde degradation rate and the CO₂ production rate by metal-photodeposited TiO₂. When the acetaldehyde was provided with dry air, the acetaldehyde degradation rate and CO₂ production rate of pure TiO₂ were larger than those of the metal-deposited TiO₂. This indicates that the deposition of metal species reduces the photocatalytic activity of TiO₂. Since the recombination of electron–hole pair is considered to be inhibited by metal deposition [8], the decrease in activity may be due to the inhibition effects on adsorption of acetaldehyde on active site of TiO₂, on formation of active species, or on interaction between active species and reactant. Further experiments should be needed to understand the inhibition effects. The slope of line in the graph is 2, which indicates the complete oxidation of acetaldehyde. The plot of Pt–TiO₂ was below the line, indicating the part of acetaldehyde was not decomposed completely into CO₂.

In the humid condition (relative humidity: 50%), the acetaldehyde degradation rate of Pt–TiO₂ was larger than that of pure TiO₂; the degradation rate of TiO₂ decreased with increasing humidity and that of Pt–TiO₂ did not change in the humidity range of 0–50%. The decrease in acetaldehyde degradation rate by TiO₂ may be due to the competitive adsorption of water and acetaldehyde, which decreased the number of adsorbed acetaldehyde. Water molecules should also inhibit the adsorption of acetaldehyde on Pt–TiO₂, how-

ever the degradation rate by Pt–TiO₂ did not decrease with increasing humidity. This suggests that the formation of active species, such as O₂^{•−} and OH[•], on Pt–TiO₂ is enhanced by water molecule. The activities of Pd–TiO₂ and Ag–TiO₂ decreased with increasing relative humidity, and the deposition of Pd and Ag did not improve the activity for acetaldehyde degradation in both the dry and humid conditions.

The effect of oxidation state of deposited metals on acetaldehyde degradation activity was analyzed. The different states of Pt, Pd, and Pt were deposited on TiO₂ by photodeposition method. The reduced forms of metal-deposited TiO₂ were prepared with methanol as reductant during the photodeposition process, and the oxidized forms were prepared without reductant while passing air instead of N₂ gas. The oxidation states of deposited metals were analyzed by XPS. As shown in the XPS spectra (Fig. 3(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 peak of Pt 4f_{7/2} for reduced form located at 70.2 eV, which is lower than the binding energy for bulk Pt but is close to the value reported in the literature for Pt–TiO₂ [14–16]. The peak of oxidized form located 72.3 eV, which was between the peak positions of PtO and Pt(O_{ads}); Pt(O_{ads}) denotes Pt with adsorbed oxygen. This suggests that the Pt formed without methanol was not reduced completely during photodeposition and combined with oxygen. In this paper the Pt combined with oxygen will be represented as Pt(O). 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. 3(b)). The main peak was due to metal Pd and the shoulder was due to PdO. When the photodeposition was performed without methanol, the major part of Pd deposited was 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. 3(c)). In the spectrum of 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.

The activities of Pt(O)–TiO₂, Pd(O)–TiO₂ and Ag(O)–TiO₂ were analyzed under humid condition using the same reactor and plotted in Fig. 4. The acetaldehyde degradation rate and the CO₂ production rate of Pt(O)–TiO₂ were 1.5 and 2.9 mmol/min, which were lower than those of Pt–TiO₂ by about 15%. This suggests that metal Pt phase has higher activity as co-catalyst for acetaldehyde degradation with TiO₂. Also, the activity of Pd(O)–TiO₂ was lower than Pd–TiO₂. Subramanian et al. reported that the charge separation efficiency of TiO₂ is increased by modification of noble metal nanoparticles, such as Au, Pt and Ir, and that the oxidation of noble metal serves the recombination center resulting in reduction of the charge separation efficiency [8]. This may be one of the reasons for the lower activity of Pt(O)–TiO₂ and Pd(O)–TiO₂ than those of Pt–TiO₂ and Pd–TiO₂. The oxidation state of Pt(O) or Pd(O) observed in

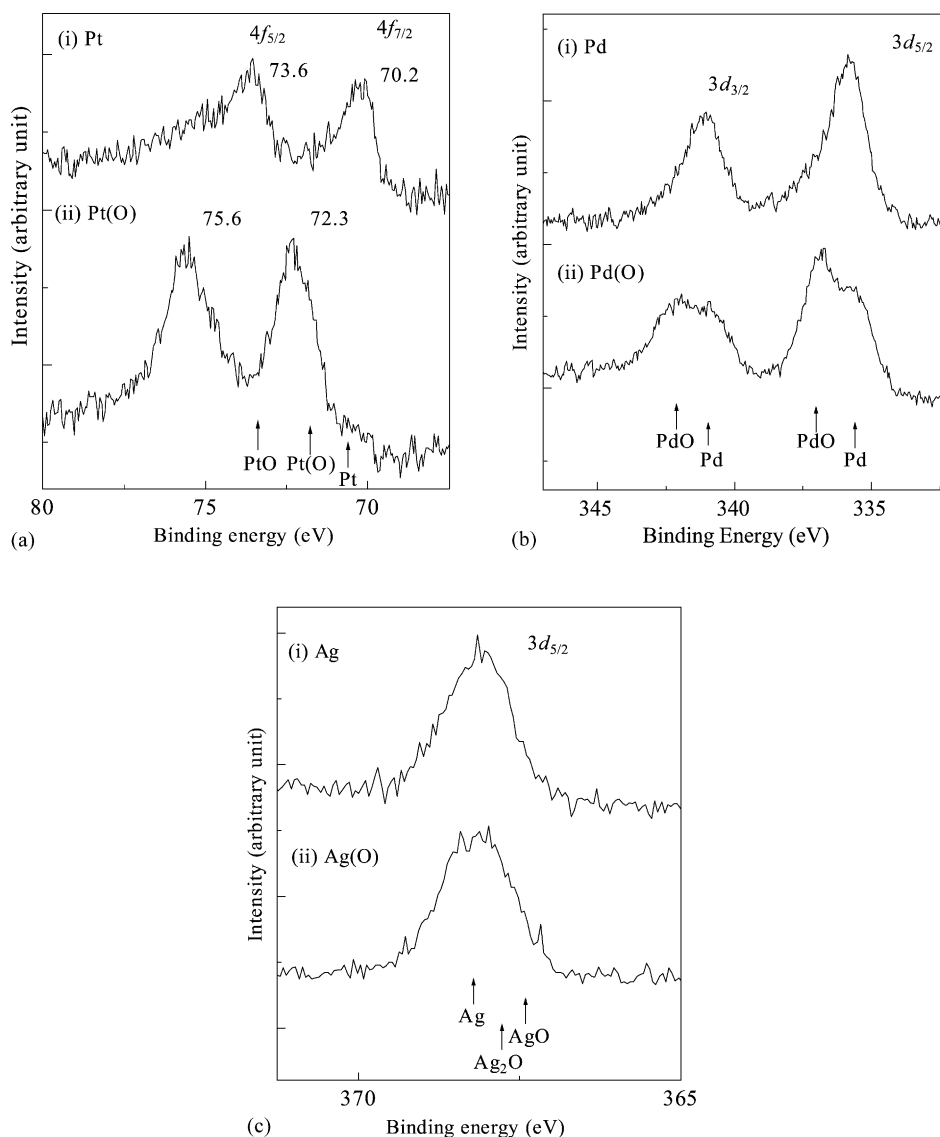


Fig. 3. XPS spectra of deposited metal species: (a) Pt–TiO₂ and Pt(O)–TiO₂; (b) Pd–TiO₂ and Pd(O)–TiO₂; (c) Ag–TiO₂ and Ag(O)–TiO₂.

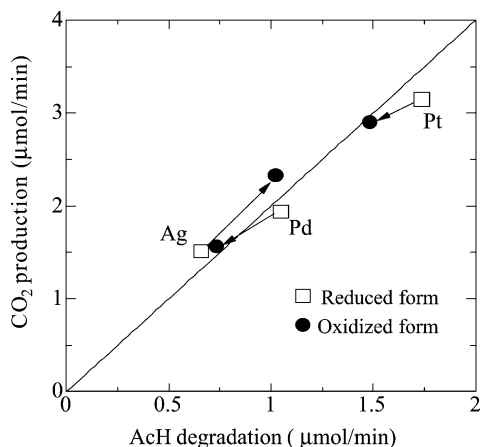


Fig. 4. Effect of oxidation state of deposited metal species on photocatalytic degradation of acetaldehyde. The amount of deposited metals were around 0.2 wt.% against TiO₂.

XPS may not always consist with the oxidation state during photocatalytic reaction under UV irradiation because electron and hole are being produced. However, it is considered that the Pt(O) on TiO₂ was not reduced to metal Pt by UV irradiation during the experimental period since the activity of Pt(O)–TiO₂, which was significantly different from that of Pt–TiO₂, did not change. At least, the Pt species derived from Pt(O) had lower effect on the enhancement of acetaldehyde degradation than metal Pt. The activity of Ag(O)–TiO₂ was significantly higher than that of the reduced form of Ag–TiO₂. The difference in the oxidation state of metal species possibly changes the several factors outside of charge separation, such as contribution of active species, adsorption of acetaldehyde, catalytic activity, etc. Therefore the evaluation of each effect is quite difficult. Here, only the formations of active species on metal- and metal oxide-deposited TiO₂ were analyzed by ESR and discussed.

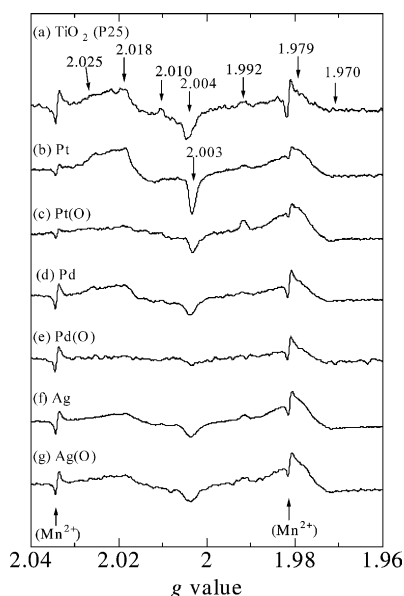


Fig. 5. ESR spectra for pure: (a) TiO_2 (P25); (b) Pt-TiO_2 ; (c) Pt(O)-TiO_2 ; (d) Pd-TiO_2 ; (e) Pd(O)-TiO_2 ; (f) Ag-TiO_2 ; (g) Ag(O)-TiO_2 recorded at 77 K under UV irradiation.

ESR spectra of the photocatalysts were recorded at 77 K under UV irradiation. In the ESR spectrum for the pure TiO_2 (Fig. 5(a)), simple signals at $g = 1.979$, 1.992 and 2.004 , and complex signals at $g = 2.007$ – 2.025 were observed. The signals were not ascribed completely, however, they seem to be a combination of signals for Ti^{3+} ($g = 1.979$ and 1.992) and O_2^- ($g = 2.004$ and 2.007 – 2.025) [17–19]. Since the TiO_2 used in this study (P25) contains two types of TiO_2 crystals, rutile and anatase, the ESR spectrum for P25 should be a complex pattern. In the ESR spectrum for Pt-TiO_2 (Fig. 5(b)), the number of signals decreased, and the intensities of signals around $g = 2.004$ and 2.018 – 2.032 increased. The intensities of peaks for Ti^{3+} did not change. These results suggest that the conditions of active species formed on Pt-TiO_2 were simplified and that the Pt deposition enhanced the formation of O_2^- or extended its lifetime, compared with pure TiO_2 . On the other hand, the signals of O_2^- on Pt(O)-TiO_2 were much smaller than those on P25 and Pt-TiO_2 . The decrease in the signal intensity of O_2^- suggests that the deposition of Pt(O) inhibits the formation of O_2^- or shortens the lifetime. This may be one of the reasons why the acetaldehyde degradation activity of Pt(O)-TiO_2 was lower than that of Pt-TiO_2 . The signals of O_2^- and Ti^{3+} for Pd(O)-TiO_2 were also smaller than that for Pd-TiO_2 significantly. PdO may strongly inhibit the formation of O_2^- or shorten the lifetime of O_2^- , and deactivate TiO_2 . The acetaldehyde degradation activities of TiO_2 with Pt and Pd species were correlated with the signal intensities of observed O_2^- . On the other hand, obvious differences were not observed in the ESR spectra of Ag-TiO_2 and Ag(O)-TiO_2 recorded at 77 K. Therefore, the difference in their activities does not depend on the O_2^- but other active species or dispersion of Ag.

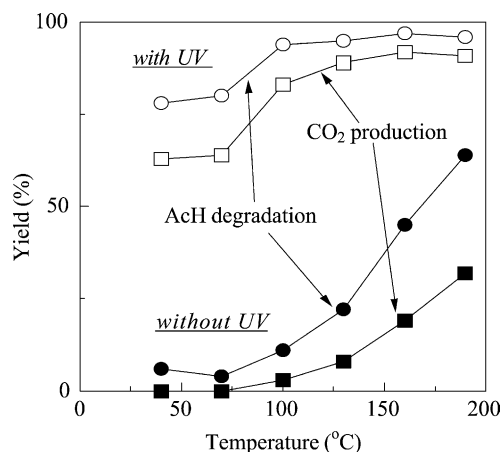


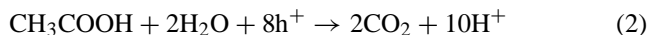
Fig. 6. Effect of temperature on photocatalytic degradation of acetaldehyde by Pt-TiO_2 (0.2 wt.%). Yield of AcH degradation and CO_2 production was calculated by (moles of AcH degraded)/(moles of AcH introduced) and (moles of CO_2 produced)/(moles of AcH introduced $\times 2$), respectively.

3.2. Effect of temperature on photocatalytic degradation of acetaldehyde

Effects of temperature on photocatalytic degradation of acetaldehyde by Pt-TiO_2 were investigated. The acetaldehyde degradation rate and the CO_2 production rate of Pt-TiO_2 and Pt(O)-TiO_2 were analyzed at the temperature between 40 and 190 °C under UV irradiation (Fig. 6). The degradation yield of Pt-TiO_2 increased from 78% (at 40 °C) to 97% (at 130 °C), and the CO_2 production yield increased from 63 to 89%. Since those yields of pure TiO_2 decreased with increasing temperature, the increase in the reaction rates for Pt-TiO_2 may be due to the thermocatalytic assist of Pt species. The degradation yield of Pt(O)-TiO_2 increased from 63% (at 40 °C) to 70% (at 130 °C), and the CO_2 production yield increased from 57 to 70%. This suggests that the thermocatalytic assist of metal Pt was stronger than that of Pt(O) . The yields of acetaldehyde degradation and CO_2 production by Pt-TiO_2 under UV irradiation did not change above 130 °C and were saturated. This is due to the lack of acetaldehyde introduced into the reactor. Further experiments using higher acetaldehyde concentration or higher gas flow rate is necessary for the discussion above 130 °C.

The acetaldehyde degradation was performed under dark condition to clarify the thermocatalytic activity of Pt on TiO_2 . Pt-TiO_2 degraded only 5% of acetaldehyde at 40 °C, however CO_2 was not formed. At 130 °C, 22% of acetaldehyde was degraded and 7% of CO_2 was produced. These results suggest that a part of acetaldehyde is degraded by Pt on TiO_2 without CO_2 formation and that UV irradiation is necessary for the complete oxidation of acetaldehyde into CO_2 . By elevating the temperature from 40 to 130 °C, the CO_2 production rate of Pt-TiO_2 under UV irradiation increased by 26% while that under dark condition increased only 7%. These results suggest that acetaldehyde was mineralized by both effects of TiO_2 photocatalyst and Pt thermocatalyst.

We are considering the following model that enhances the degradation of acetaldehyde by thermocatalytic assist. Only UV irradiation is applied, the formed active oxygen species are consumed for both of oxidation of acetaldehyde into acetic acid (Eq. (1)) and acetic acid into CO₂ (Eq. (2)):



The contributions of e⁻ and O₂ are also possible. If the oxidation of acetaldehyde into acetic acid is thermocatalytically possible at the elevated temperatures, active oxygen species produced by UV irradiation may be consumed mainly for the oxidation of acetic acid into CO₂ only, and the total reaction rate will increase. When the Pt–TiO₂ was contacted with acetaldehyde (100 ppm) at 190 °C without UV irradiation for 3 h and washed with distilled water, 43 mmol of acetic acid was detected by ion chromatography. This value corresponded to 6% of introduced acetaldehyde, and the contribution of thermocatalytic formation of acetic acid to the above model seems to be possible.

4. Conclusion

Only the deposition of metal Pt on TiO₂ increased the acetaldehyde degradation activity in the humid condition, however the deposition of other metals and metal oxides decreased the activity. The ESR measurements suggest that the difference in activity of metal- and metal oxide-deposited TiO₂ is due to the amounts of O₂⁻ formed by UV absorption. A part of acetaldehyde was degraded thermocatalytically by Pt on TiO₂ without CO₂ formation at 70–190 °C, and UV irradiation is necessary for mineralizing acetaldehyde completely. The mineralization of acetaldehyde is considered to be enhanced by the partial oxidation of acetaldehyde by Pt thermocatalyst and the oxidation of intermediates into CO₂ by TiO₂ photocatalyst at temperature above 70 °C. Since these temperatures are easily obtained by concentrating so-

lar light, the application of thermocatalytic assist seems to be possible without impairing the energy-saving merit of photocatalyst.

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