

Article

Photocatalytic Oxidation Processes for Toluene Oxidation over TiO₂ Catalysts

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Abstract: Gas-solid heterogeneous photooxidation of toluene over TiO₂ catalyst was studied to investigate the factors controlling the catalytic activities. The toluene photooxidation behavior on TiO₂ was strongly affected by the formation and oxidation behavior of intermediate compounds on TiO₂, and their accumulation decreased the reaction rate for toluene photooxidation. The formation and oxidation behavior of the byproduct compounds depended on the initial concentration of toluene and water vapor. *In situ* Fourier transform infrared (FTIR) studies revealed that water vapor promoted the cleavage of the aromatic ring and facilitated CO₂ formation. At the reaction temperature of 300 K, the deposition of Pt on TiO₂ suppressed CO formation, whereas catalytic activity was decreased due to the increase in the amount of intermediate compounds. On the other hand, Pt/TiO₂ showed higher activity than TiO₂ at 353 K, in spite of the increase of the intermediate compounds.

Keywords: titanium dioxide; photocatalytic reaction; oxidation; toluene

1. Introduction

Control of air quality is still one of the important topics in the research area of environmental science and technology. Photocatalytic oxidation (PCO) processes have been extensively studied for air quality control when the target compounds are CO, NO, volatile organic compounds (VOCs) and

bioaerosols in closed environment [1–5]. PCO is effective for the control of these compounds, especially under their diluted conditions. In the case of VOC removal from polluted air, TiO₂ catalysts have been generally used because of their high activities, high safety and low cost. The photooxidation behavior of various kinds of organic compounds, including aromatic compounds on near UV irradiated TiO₂ catalysts, has been clarified [6–19].

It has been generally accepted that the factors controlling photocatalytic activities involve the efficiency for electron-hole pair generation and their separation, formation of active oxygen species on the TiO₂ surface and their reaction with organic compounds adsorbed on the surface [1,19]. Therefore, many efforts have been made to improve the photocatalytic properties of TiO₂ catalysts by controlling their crystallinity, band gaps and surface area. The other catalyst-modification methods are metal doping/deposition in/on the TiO₂ catalyst surface [20,21]. Deposition of Pt metals on TiO₂ was effective in improving the rate for VOC photooxidation when the photoreaction was conducted with heating processes [22,23].

We have carried out the photocatalytic oxidation of hydrocarbons with TiO₂ to investigate their photooxidation behavior by using a gas-solid heterogeneous flow system [24–28]. Benzene and toluene were oxidized to CO₂ on TiO₂ under near-UV irradiation; the TiO₂ catalysts suffered from severe deactivation when aromatic compounds were used as the substrate under their high concentrations or dry conditions [7,9]. Under these conditions, intermediate compounds, including oxygen-containing species and carbonaceous materials, were generally formed on the TiO₂ catalyst surface, which covered catalytic active sites, inhibiting the adsorption and oxidation of toluene on the sites. On the basis of these findings, we have suggested that the formation and oxidation behavior of such intermediate compounds is also one of the important factors that controls the photocatalytic activities [26].

We herein report the photocatalytic oxidation of toluene over TiO₂ catalysts by focusing on the formation and oxidation behavior of intermediate compounds on the catalyst surface. The amount of intermediate compounds on TiO₂ was compared under various conditions to investigate the relationship between the photooxidation behavior of toluene and that of intermediate compounds in detail. We also conducted *in situ* Fourier transform infrared (FTIR) spectroscopic studies for toluene photooxidation on TiO₂ to reveal the effect of water vapor on the behavior of toluene and the intermediate compounds.

2. Results and Discussion

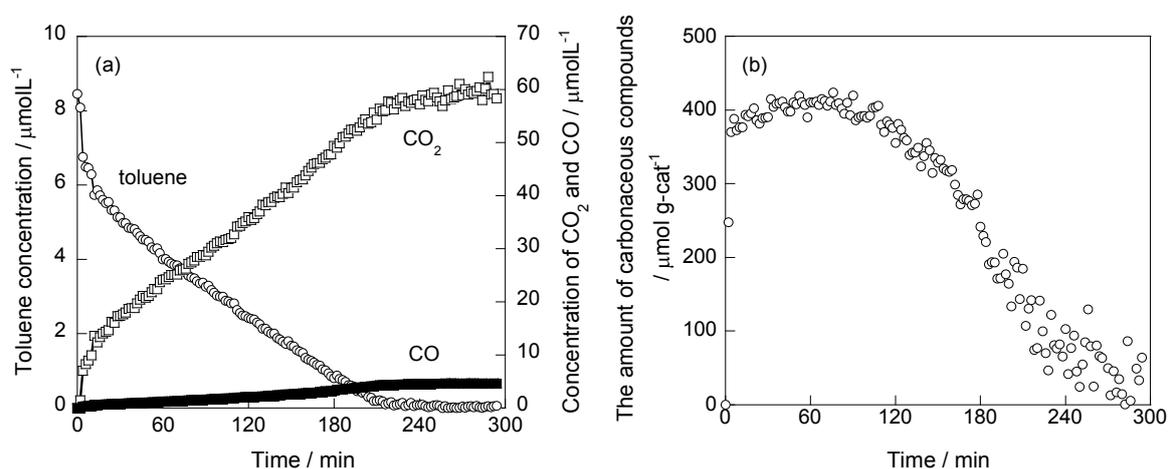
2.1. Photooxidation Behavior of Toluene on TiO₂

Figure 1a shows the time course for toluene photooxidation with TiO₂ under humid condition ([toluene]₀ = 8.4 μmol/L (210 ppmv), [H₂O] = 1.0%) with a circulation system at 300 K. After the adsorption-desorption equilibrium was achieved in dark, photoirradiation was started for the TiO₂ catalyst. Toluene was oxidized on TiO₂ to form CO₂ and CO without an induction period on irradiation. Toluene concentration rapidly decreased in the initial period (~4 min), and then, the reaction rate decreased to a constant value until gaseous toluene was almost completely consumed. The formation of these intermediate compounds on TiO₂ in toluene photooxidation has been reported and

the oxygen-containing byproducts, such as benzoic acid and benzaldehyde, have been identified [15]. The formation of carbonaceous species was also confirmed by browning of TiO₂ catalyst during the toluene photooxidation. Figure 1b shows the time course for the changes in the amount of byproduct compounds on TiO₂, which can be estimated from the balance between the amount of toluene consumption and that of CO_x formation, as expressed by Equation (1), where V and W are the volume of the circulation system and catalyst mass. This estimation was valid, because no other C-containing byproducts were observed in gas phase with our system, indicating that the byproducts were presented on the catalyst surface.

$$\text{The amount of intermediate compounds on the catalyst surface} = \{([\text{toluene}]_0 - [\text{toluene}]) \times 7 - [\text{CO}_2] - [\text{CO}]\} \times \frac{V}{W} \quad (1)$$

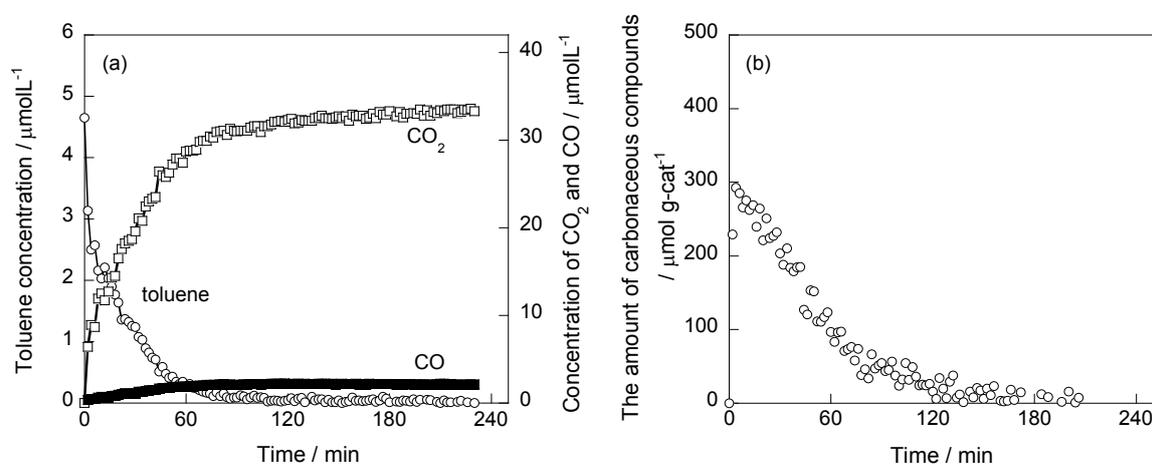
Figure 1. Time course for toluene photooxidation with TiO₂. (a) Changes in concentration of toluene, CO₂ and CO; (b) Changes in the amount of intermediate compounds on TiO₂. [toluene]₀ = 8.4 μmol/L, [H₂O] = 1.0%, [O₂] = 20%.



The amount of byproduct compounds greatly increased in the initial period. The amount reached the maximum at 76 min, where the amount of byproducts and the C-density on TiO₂ were estimated to be 423 μmol/g-catalyst and 4.7 C-atom/nm², respectively, indicating that the catalysts were significantly covered by the intermediate compounds. Comparison of the behavior of intermediate compounds with that of toluene indicates that the build-up of the byproducts caused the decrease in the reaction rate by blocking the catalyst active sites in the initial period. The intermediate compounds then gradually decreased with time, and their amount reached almost zero after 300 min, indicating that these compounds were further oxidized to CO₂ and CO during the reaction.

The formation behavior for these intermediate compounds greatly depended on the initial concentration of toluene in gas phase. When the toluene concentration was decreased to 4.2 μmol/L (Figure 2a), the toluene concentration monotonically decreased with time on photoirradiation. In this case, a similar trend was observed in the initial period of the reaction: the rate for toluene photooxidation significantly decreased due to the formation of intermediate compounds on TiO₂ (Figure 2b). However, the amount of intermediate compounds was lower and decreased monotonically with time.

Figure 2. Time course for toluene photooxidation with TiO₂. (a) Changes in concentration of toluene, CO₂ and CO; (b) Changes in the amount of intermediate compounds on TiO₂. [toluene]₀ = 4.6 μmol/L, [H₂O] = 1.0%, [O₂] = 20%.



It has been reported that the rate of toluene photooxidation on TiO₂ catalyst can be fitted to Langmuir-Hinshelwood (L-H) kinetics, Equation (2), where k and K are a constant and the equilibrium constant for toluene adsorption on TiO₂, respectively [16]:

$$-\frac{d[\text{toluene}]}{dt} = \frac{kK[\text{toluene}]}{1 + K[\text{toluene}]} \quad (2)$$

In the present study, however, the decay in toluene concentration was not fitted to the kinetic equation. This discrepancy was ascribed to the reaction condition. When the intermediate compounds were formed on TiO₂ surface, the catalytic active sites were poisoned by these compounds, and the fraction of surface coverage of toluene (θ in Equation (3)) decreased. Hence, the reaction rate did not obey the L-H kinetics under the condition where the catalyst surface was significantly covered with the intermediate compounds.

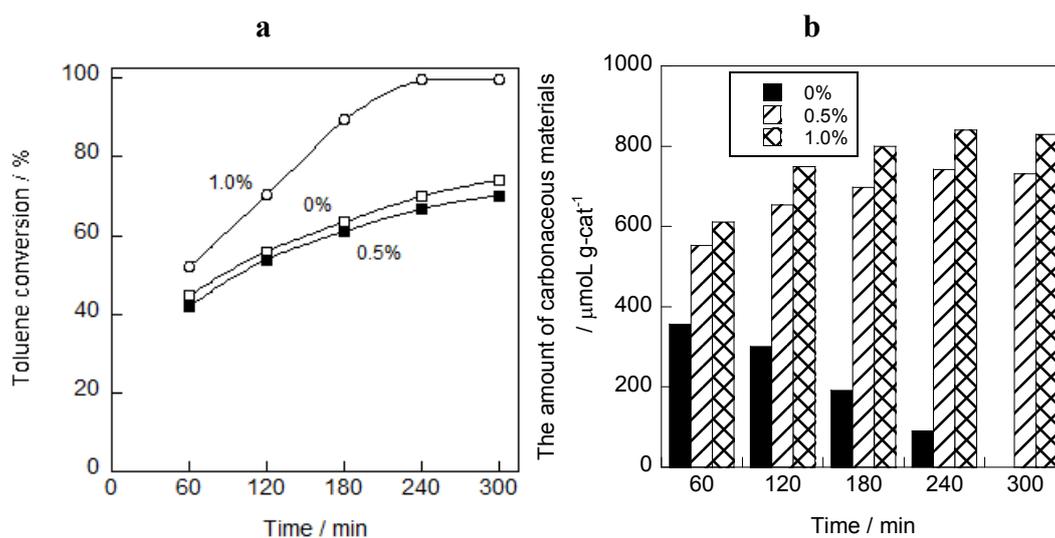
$$\theta = \frac{K[\text{toluene}]}{1 + K[\text{toluene}]} \quad (3)$$

The formation mechanism of the intermediate compounds on TiO₂ in toluene photooxidation has been already studied by many groups [10,11,13,15]. It is well accepted that electron-hole pairs photoformed on TiO₂ diffused to surface sites and generated active oxygen species [1,2]. So, the highly-reactive species attacked the aromatic ring of toluene to form organic radicals, which were then oxidized by molecular O₂ to peroxy radicals, leading to the formation of ring-opening compounds. The methyl groups were also oxidized by the active oxygen species to form benzoic acid. When toluene concentration increased, the intermediate radicals also reacted with toluene to form dimerized species, which were then transformed to oligomeric and polymeric species in the presence of toluene. They were the first step for the formation of carbonaceous materials on TiO₂. As mentioned above, however, these compounds were further oxidized to CO₂ and CO under photoirradiation.

The formation behavior of the intermediate compounds was also greatly affected by the concentration of water vapor in gas phase, as reported earlier [9]. Figure 3 compares the time course plots for toluene conversion, CO_x formation and the amount of byproduct compounds on TiO₂ under

different humidity conditions. Water vapor in reaction gas have both positive and negative effects on toluene photooxidation. As a positive effect, water vapor inhibited the build-up of intermediate compounds on TiO_2 , giving rise to the increase in toluene photooxidation activity [24,26]. On the other hand, it inhibited the adsorption of toluene on the TiO_2 surface, leading to the decrease in toluene photooxidation activity. At the concentration of 0.5%, the two effects competed, and the former effect was prominent at 1.0%. The positive effect of water vapor was explained in terms of radical species: OH radicals were formed on the TiO_2 surface by photoirradiation in the presence of water vapor. However, this mechanism has been questioned because of the low reactivity of OH radicals on TiO_2 [29]. In addition, no evidence was obtained for the formation of OH radicals on the gas-solid heterogeneous TiO_2 photooxidation system. Further investigation should be conducted to reveal the reaction mechanism.

Figure 3. Effect of humidity on toluene photooxidation with TiO_2 . (a) Time course for toluene conversion; (b) Changes in the amount of intermediate compounds on TiO_2 . $[\text{toluene}]_0 = 8.4 \mu\text{mol/L}$, $[\text{O}_2] = 20\%$.

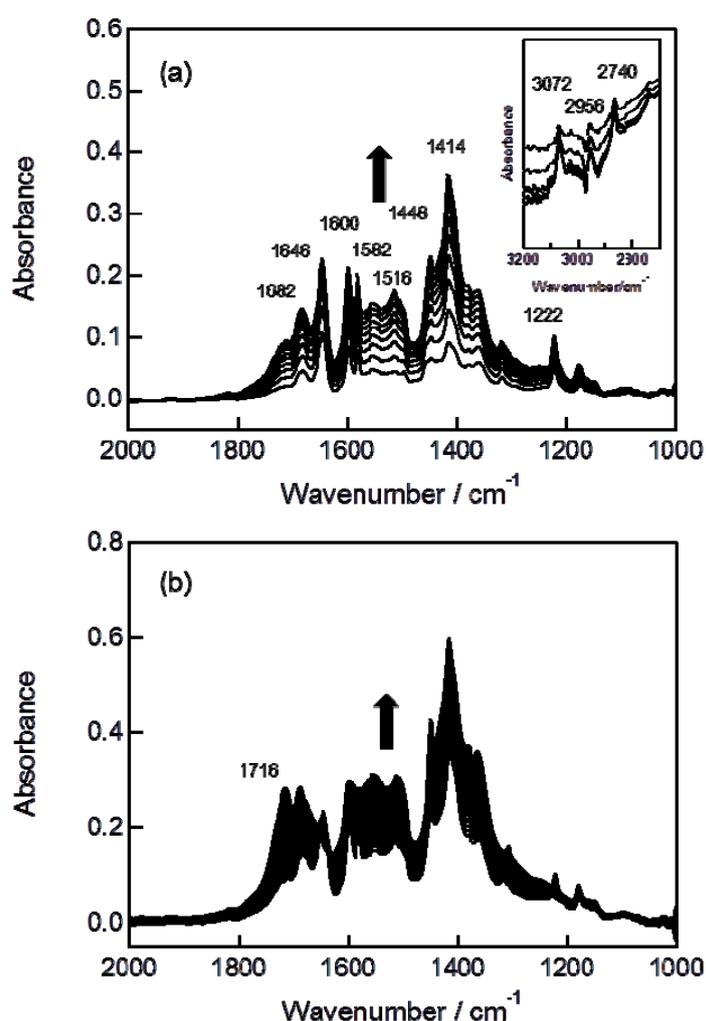


2.2. In Situ FTIR Studies for Toluene Photooxidation

In situ FTIR studies were conducted to pursue the photooxidation behavior of toluene on TiO_2 and, especially, to investigate the effect of water vapor on toluene photooxidation. Figure 4 shows the changes in FTIR spectra of intermediate compounds on TiO_2 during toluene photooxidation in air in the absence of water vapor. Here, it should be noted that the reaction rate was much lower than that in Figure 1, because the catalyst weight was much lower (see Experimental Section). In the toluene photooxidation ($[\text{toluene}]_0 = 30 \text{ ppm}$), the bands appeared in the wavenumber range $1000\text{--}2000 \text{ cm}^{-1}$ (Figure 4a). In the initial period of reaction (0~5 h), the bands due to various kinds of intermediate compounds were observed. The bands at 1222 , 1582 , 1646 and 1682 cm^{-1} were assignable to benzaldehyde [30–34]. The strong band at 1414 cm^{-1} and the bands at 1448 and 1516 cm^{-1} were assignable to adsorbed benzoic acid on TiO_2 [30–34]. The formation of these oxygen-containing compounds indicated that the active oxygen species attacked toluene and the intermediate compounds on the catalyst surface. In a prolonged reaction, the intensities of these bands increased with time,

implying that the intermediate compounds were continuously accumulated on the TiO₂ catalyst surface (Figure 4b). These behaviors were consistent with those observed for catalytic reactions described in Section 2.1. Then, the bands in the range of 1680–1720 cm⁻¹, which were assignable to C=O stretchings, increased in their intensities. The appearance of the band at 1716 cm⁻¹ due to aliphatic C=O groups indicated that aromatic ring cleavage occurred for the byproduct compounds. The bands at 2740, 2956 and 3072 cm⁻¹ appeared, and their intensities increased with time, indicating that aromatic and aliphatic C–H groups were present in the intermediate compounds.

Figure 4. Fourier transform infrared (FTIR) spectral changes in TiO₂ catalyst surface during toluene photooxidation under dry condition. Spectra were taken at 0.5 h intervals. (a) 1–5 h, (b) 5.5–40 h [toluene]₀ = 0.12 μmol/L, [O₂] = 20%.

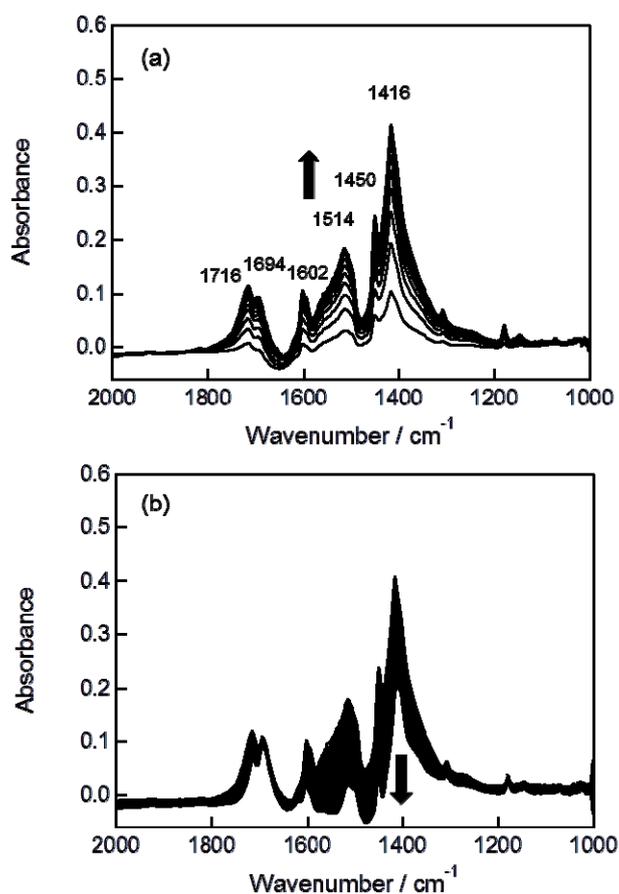


On the other hand, the intermediate compounds formed on TiO₂ in the presence of H₂O ([toluene] = 0.12 μmol/L (30 ppmv), [H₂O] = 1.0%) were much different, as shown in Figure 5. After photoirradiation, the bands due to intermediate compounds were also observed. Although the bands due to the adsorbed benzoic acid (1416, 1450, 1514 and 1602 cm⁻¹) were observed, the bands due to benzaldehyde were not detected, indicating that the oxidation of benzaldehyde to benzoic acid was promoted by the presence of water vapor. The difference was more prominent for the band of aliphatic C=O groups (1716 cm⁻¹). The band appeared in the initial period in the presence of water vapor, in

marked contrast with the reaction in the absence of water vapor, where there was an induction period for the appearance of the band. Therefore, benzene ring-cleavage immediately proceeded when water vapor was present in the reaction gas. The intensities of these bands increased with time until 5 h, and then, the intensities decreased with time, indicating that these intermediate compounds were oxidized to CO_2 and CO under photoirradiation in the presence of water vapor.

In the toluene photooxidation, active oxygen species photoformed on the TiO_2 oxidize methyl group to form benzaldehyde and benzoic acid. The oxidation of aromatic rings gives rise to the formation of phenols or cleavage of the aromatic rings, which is the first step for complete oxidation to CO_2 . The findings described above show that the presence of water vapor promoted the sequential oxidizing of benzaldehyde to benzoic acid and the cleavage of aromatic rings. Therefore, the accumulation of the intermediate compounds was greatly suppressed by the presence of water vapor.

Figure 5. FTIR spectral changes in TiO_2 catalyst surface during toluene photooxidation under humid condition. Spectra were taken at 0.5 h intervals. (a) 1–5 h; (b) 5.5–40 h. $[\text{toluene}]_0 = 0.12 \mu\text{mol/L}$, $[\text{O}_2] = 20\%$. $[\text{H}_2\text{O}] = 1.0\%$.

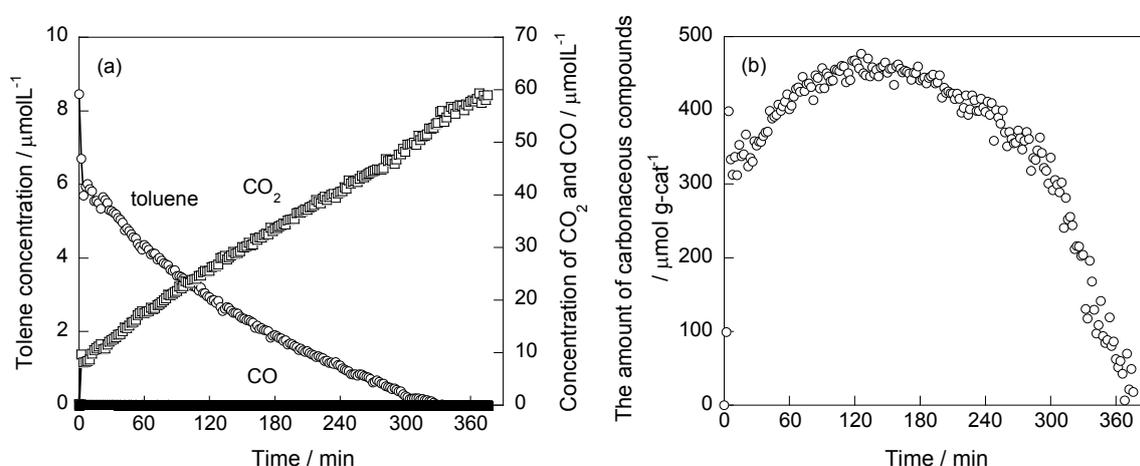


2.3. Effect of Pt Deposition and Catalyst Heating

Platinization of TiO_2 is one of the effective methods to improve the photocatalytic oxidation activities, because it is reported to suppress the recombination of the electron-hole pair formed by photoirradiation in TiO_2 . In the case of benzene oxidation, the deposition of Pt did not change the rate for benzene photooxidation on TiO_2 [25]. Figure 6 shows time course plots for toluene conversion,

CO_x formation and the amount of intermediate compounds on Pt/TiO₂ catalyst. Toluene concentration monotonically decreased with time, and the profile was similar to that with TiO₂ (Figure 1). However, the amount of intermediate compounds formed on Pt/TiO₂ was much larger than that on TiO₂. Pt/TiO₂ catalyst showed lower activity than TiO₂ due to the increase in the amount of intermediate compounds on the catalyst. The intermediate compounds existed on the catalyst even after toluene was completely consumed (300~360 min). Thus, deposition of Pt on TiO₂ promoted the formation of intermediate compounds at room temperature.

Figure 6. Time course for toluene photooxidation with Pt/TiO₂. (a) Changes in concentration of toluene, CO₂ and CO; (b) Changes in the amount of intermediate compounds on Pt/TiO₂. [toluene]₀ = 8.4 μmol/L, [H₂O] = 1.0%, [O₂] = 20%.

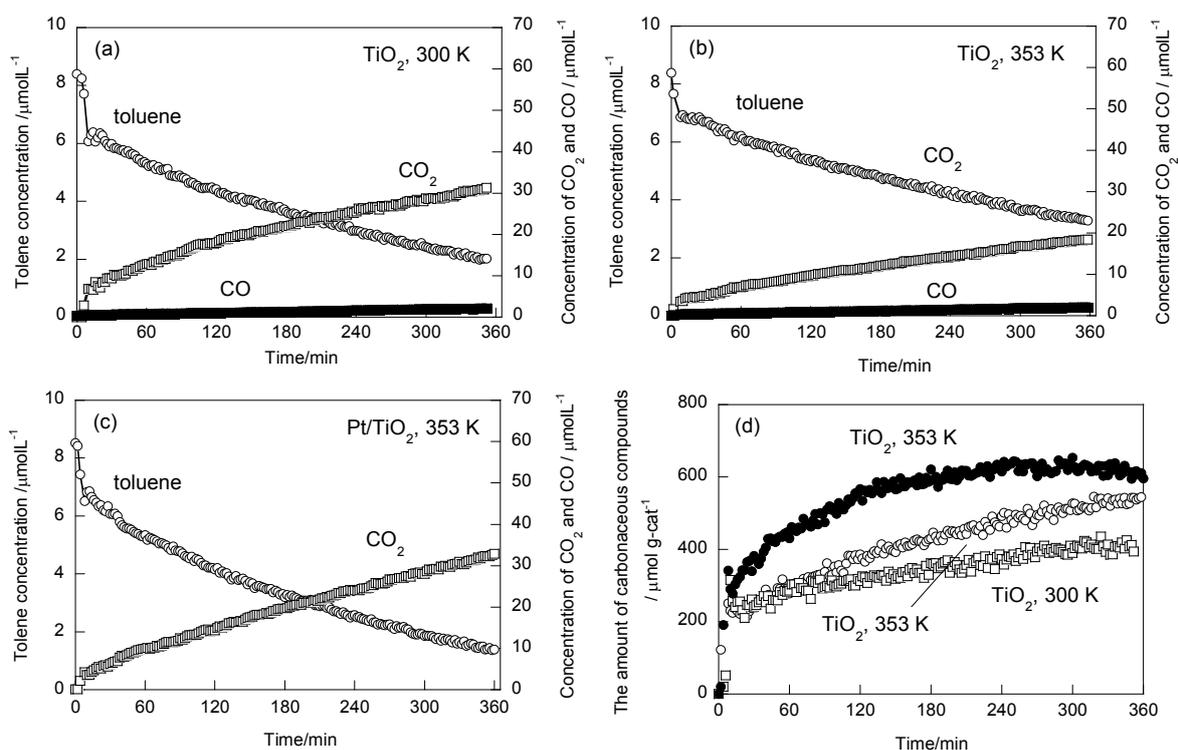


On the other hand, CO formation was greatly suppressed when the Pt/TiO₂ catalyst was used for the reaction. CO was in all cases detected in toluene photooxidation on TiO₂ catalyst, even when the reaction conditions were variously changed. However, CO concentration greatly decreased with Pt/TiO₂ catalyst. This behavior was ascribed to the facile oxidation of CO on Pt/TiO₂. The byproduct CO was oxidized on Pt sites under photoirradiation at room temperature [35]. This finding also indicates that the Pt sites were not significantly poisoned by the intermediate compounds, and thus, they can contribute to the CO photooxidation.

In our circulation recycling system, Pt/TiO₂ catalysts were effective under briefly heated condition. Figure 7 shows time course plots for toluene photooxidation over TiO₂ and platinumized catalyst (1 wt%-Pt/TiO₂) at 353 K. Here, the reaction rate was much lower than that in Figure 1, because a different kind of photochemical reactor was used for toluene photooxidation (see Experimental Section). Photocatalytic activity of TiO₂ decreased and the amount of intermediate compounds increased by heating the catalyst up to 353 K. This behavior was ascribed to the decrease in H₂O adsorption capacity of TiO₂ at elevated temperature, which resulted in the promotion of the accumulation of intermediate compounds on TiO₂. On the other hand, Pt deposition on TiO₂ increased the toluene photooxidation at the same reaction temperature, although the amount of intermediate compounds formed on Pt/TiO₂ was larger than that on TiO₂. Pt/TiO₂ catalyst was also effective for

suppression of CO formation at 353 K, because CO concentration was lower than the detection limit (<3 ppm).

Figure 7. Time course for toluene photooxidation with TiO₂ and Pt/TiO₂. (a) Changes in concentration of toluene, CO₂ and CO on TiO₂ at 300 K; (b) on TiO₂ at 353 K and (c) on Pt/TiO₂ at 353 K; (d) Changes in the amount of intermediate compounds on TiO₂ and Pt/TiO₂. [toluene]₀ = 8.4 μmol/L, [H₂O] = 1.0%, [O₂] = 20%.



3. Experimental Section

3.1. Catalyst Materials

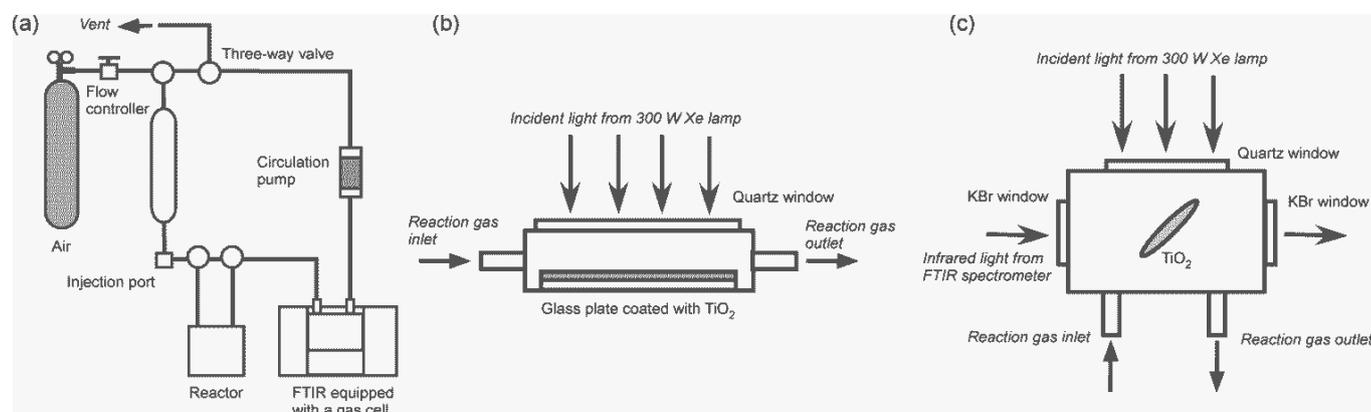
Commercially available TiO₂ (P25; Nippon Aerosil Co. Ltd.; Tokyo, Japan) supplied from Catalysis Society of Japan as JRC-TIO-4) was used as catalyst and precursor of Pt/TiO₂ catalyst. The BET surface area was 54 m²/g. Pt deposition on TiO₂ was carried out by the photodeposition method, according to the procedure reported earlier [25,35]. The Pt loading was 1.0 wt%. CO chemisorption measurements revealed that Pt dispersion of Pt/TiO₂ was 16%.

3.2. Photocatalytic Test Reaction

Photoreactions were carried out with a circulation system (Figure 8a). The total volume of the system was 3.5 L. The photochemical reactor was fabricated from a Pyrex glass tube with a quartz glass window and contained a square-shaped glass plate (50 mm × 45 mm) (Figure 8b). The catalyst was coated on one side of the glass plate from an aqueous slurry of catalyst powder and dried at 383 K. Catalyst weight on the plate was 0.10 g. Photoirradiation was carried out for the catalyst through the quartz glass window by a 300 W Xe lamp equipped with a UV-30 cut filter ($\lambda > 300$ nm). Reaction

gases were prepared by mixing toluene vapor with pure air. When reactions were carried out under humidified conditions, toluene and water vapor were introduced to the reaction gases with a syringe from the injection port. The reaction temperature was around 295 K. As a pretreatment, the catalyst was photoirradiated in air to decompose the organic impurities adsorbed on the TiO₂ surface. After the gas-solid adsorption equilibrium of the substrate was achieved in the reactor, photoirradiation was started. The circulating flow rate was 2.0 L/min. Concentrations of toluene, CO₂ and CO were simultaneously determined by an FTIR spectrometer (PerkinElmer Spectrum One) equipped with a gas cell (2.4 m path length, 0.20 L volume).

Figure 8. Schematic of photocatalytic reaction system and equipment for catalytic reaction and FTIR measurement. (a) Photocatalytic system; (b) reactor for toluene photooxidation and (c) *in-situ* FTIR cell.



In the case of catalytic toluene photooxidation under heated condition, a photochemical reactor with a cylindrical shape was used. The catalysts were loaded on a glass plate with the area of 9 cm² (3 cm × 3 cm) and then mounted in the photochemical reactor. A ceramic heater was contacted with the bottom side of the reactor to control the reaction temperature. This system can identify organic byproduct at the ppm level. Carbon balance was defined as 7-times the amount of the CO₂ (and CO) formed and divided by the amount of toluene reacted.

3.3. FTIR Studies

FTIR spectra of catalysts were measured on an FTIR spectrometer (PerkinElmer Spectrum One) equipped with a TGS detector and an *in situ* FTIR cell, which was connected to the circulation recycling system described above. The cell had a quartz glass window on the top and a set of connectors to allow reaction gases to flow through the cell (Figure 8c). On both sides of the cell, KBr windows were placed. TiO₂ samples were pressed into thin disk (20 mm Φ in diameter) and placed in the cell. Photoirradiation was carried out with a 300 W Xe lamp equipped with a UV-30 cut filter from the quartz window. The catalyst sample was photoirradiated through the quartz window. FTIR spectra were taken from the KBr windows. Prior to the FTIR measurements, the catalyst sample was photoirradiated in humidified air.

4. Conclusions

In this study, we investigated the toluene oxidation behavior on photoirradiated TiO₂ by using a circulation recycling system with a near-UV light source ($\lambda > 300$ nm). The amount of intermediate compounds on TiO₂ was estimated, and their formation/oxidation behavior was compared with toluene photooxidation behavior. Water vapor in the reaction gas promoted the oxidation of these intermediate compounds to CO₂ and CO. FTIR studies showed that various kinds of oxygen-containing byproducts were formed in toluene photooxidation. The aliphatic C=O groups were formed without an induction period in the presence of water vapor, whereas there was a much longer induction period for their formation, revealing that the cleavage of the aromatic ring was promoted in the presence of water vapor. In the present system, deposition of Pt particles on TiO₂ has a detrimental effect on toluene photooxidation activity at room temperature (300 K). The amount of intermediate compounds on Pt/TiO₂ was higher than that with TiO₂ catalyst, and the rate for their oxidation to CO₂ was much lower. However, Pt deposition was effective for suppression of CO formation. When the catalyst was heated at 353 K, Pt/TiO₂ showed higher activity for toluene photooxidation than TiO₂, although the intermediate compounds also increased by Pt deposition.

Conflict of Interest

The authors declare no conflict of interest.

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