Complete Decomposition of Benzene, Toluene, and Particulate Matter Contained in the Exhaust of Diesel Engines by Means of Thermally Excited Holes in Titanium Dioxide at High Temperatures

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We previously reported on a decomposition system of organic wastes by the use of thermally excited holes in TiO_2 at high temperatures. A good feature of our system is that it makes use of a large number of holes formed, for example, at 350°C for the oxidation of organic wastes. In this investigation, we aim at applying this technology to the complete decomposition of benzene, toluene, and particulate matter (PM) included in the exhaust of diesel engines. Special attention has been paid to the adsorption process of benzene and toluene onto the surface of TiO_2 , as well as to their subsequent decomposition, as studied by thermal analysis, Raman spectroscopy, and ESR in consideration of the specific surface of TiO_2 powders. Both benzene and toluene are found to completely decompose into H_2O and CO_2 at about 350°C , via fragments of ethylene, butene, propene, and butadiene. On the other hand, PM appears more difficult to decompose due to its powdered form. However, PM was finally confirmed to be decomposed when the mixture of PM and TiO_2 was heated under a pressure of about 280 N/m^2 at about 350°C . [DOI: 10.1143/JJAP.46.6037]

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1. Introduction

We have previously reported on a complete decomposition system of polycarbonates (PC; used as substrates for optical disks) that utilizes thermally excited holes in TiO_2 at high temperatures.^{1–3)} The above investigation has been initiated in view of the serious problem on how to dispose used optical disks. Our decomposition system is similar to the photocatalytic system that makes use of photogenerated holes for the oxidation decomposition of various substances. However, our system differs distinctly in the utilization of thermally excited holes at high temperatures (for example, at about 350°C) in combination with a molten state of PC, as shown in Fig. 1. A large number of charge carriers are available in TiO_2 at high temperatures as shown by the product of the Fermi-Dirac distribution function and the density of states.⁴⁾ The number of carriers at room temperature (RT) and 350°C [$n_{\text{RT}} = n_0 \exp(-E_g/2kT_{\text{RT}})$ and $n_{623\text{K}} = n_0 \exp(-E_g/2kT_{623})$, respectively] gives a ratio of $n_{623\text{K}}/n_{\text{RT}} \approx 8.8 \times 10^{13}$, where $E_g = 3.2\text{ eV}$. This number has approximately been confirmed in our previous experiment based on the single crystals of TiO_2 of the rutile phase.³⁾ In addition, PC melts into liquid at these temperatures to form the “solid (TiO_2)/liquid (molten PC)” interface. This enables us to successively decompose PC into small fragments, followed by complete combustion with oxygen to yield solely H_2O and CO_2 .²⁾ To date, we have shown that all kinds of thermoplastic resins and thermosetting polymers (i.e., three-dimensional polymers that have no melting point) can completely be decomposed.³⁾ We have also confirmed that any types of semiconductors can basically work as an alternative for TiO_2 if they are stable in air at high temperatures.³⁾ Among these, however, TiO_2 is still the best material at present. The mechanism of decomposition has also been clarified to proceed in such a way that radicals are initially formed in PC by thermally generated holes and then propagate throughout the material to break up PC into fragments, ending up with their complete combustion with oxygen to yield H_2O and CO_2 (Fig. 1).³⁾ These results prompted us to believe that even

benzene, toluene, and particulate matter (PM) included in the exhaust of diesel engines can be decomposed by this technology. Diesel engines have been widely used for trucks, passenger cars, vessels, heavy machineries, and so on. Diesel engines are characterized by various factors such as a high thermal efficiency of about 45–50%, which is higher than that in gasoline engines by about 10–15%, as well as high torque, robustness, and low fuel consumption among others. On the other hand, the main drawback of diesel engines lies in their exhaust comprising mainly hydrocarbons (benzene, toluene, etc.), PM, and NO_x . PM is a carbonlike, black powder comprising aromatic and aliphatic hydrocarbons and sulfates. In this study, we focus on the complete decomposition of benzene, toluene, and PM.

2. Experiment

2.1 Materials

TiO_2 powders of ST01 (anatase form) and CR80 (rutile form) were obtained from Ishihara Sangyo (ISK). ST01 is an active TiO_2 and it is designed for photocatalysts with a specific surface of about $278\text{ m}^2/\text{g}$ and a grain size of about 7 nm. On the other hand, CR80 is a surface-coated TiO_2 used widely as a white pigment and as an inert reference in this investigation together with $\alpha\text{-Al}_2\text{O}_3$ (Junsei Chemical). All powdered samples were calcinated in air at 500°C for 1 h before use. Due to this calcinations, the specific surface of ST-01 was decreased from 278 to $96\text{ m}^2/\text{g}$; however, it remains nearly unchanged with further calcination. On the other hand, no noticeable change was recognized in CR80 and $\alpha\text{-Al}_2\text{O}_3$. Benzene and toluene of GR grade were purchased from Wako Pure Chemical Industries. PM powders were supplied by ISUZU Advanced Engineering Center.

2.2 Autoclave used for decomposition of benzene and toluene

An autoclave equipped with a mass spectrometer was particularly designed for this experiment. The schematic representation is shown in Fig. 2. The volume of the reaction vessel is 300 ml, in which 40 g of TiO_2 , or CR80 or $\alpha\text{-Al}_2\text{O}_3$ was charged. The stirrer rotates at a rate of 150 rpm. Gases

Fig. 1. Decomposition of PC at “TiO₂/PC” interface by thermally generated holes.

Fig. 2. Schematic representation of autoclave used for decomposition experiments. Q-mass denotes a quadrupole mass spectrometer.

(benzene or toluene) were introduced, using air or N₂ as the carrier gas, into the reaction vessel from the bottom of the autoclave through a sintered filter of stainless steel powders. Benzene or toluene-saturated vapors were prepared by bubbling either air or N₂. The concentrations of benzene and toluene were 3.03 and 2.28% relative to air, respectively. The gas flow rate was controlled at 200 ml/min; whereas the temperature was varied in the range between 100 and 500 °C. The outgas was sampled at various temperatures and analyzed by mass spectrometry.

2.3 Sampling of the intermediate: benzene/TiO₂ and toluene/TiO₂

To study the intermediates in the decomposition process, *ca.* 100 mg of TiO₂ powders was extracted from the reaction vessel every 50 °C *in situ* in the temperature range from 100 to 500 °C. These samples were brown and highly viscous due to reactions between the adsorbate (benzene or toluene) and the adsorbent (TiO₂), as described later in §3.2.

2.4 Decomposition of PM

Two kinds of samples were prepared for the decomposition test. Sample 1 is a mixture of 1.0 mg of PM (black

powder) with 50 mg of ST01 (white powder) ground in a mortar with a pestle. Sample 2 is a tablet prepared by pressing sample 1 with a pressure of 280 N/m². PM/CR80 samples were also prepared as reference with the same composition.

2.5 Equipment for measurement

DSC 8230 and TGA 8120 from RIGAKU were used for measurements of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. The heating rate was 10 °C/min in both measurements. Raman spectra were measured using a NRS-3100 laser Raman spectrophotometer from JASCO. Measurements of electron spin resonance (ESR) were carried out using a JES-FA200 from JEOL. ESR signals were corrected by Mn markers and radical concentrations were estimated on the basis of the concentration of α,α' -diphenyl- β -picrylhydrazyl (DPPH) used as the reference. A quadrupole mass spectrometer (model RG-102 from ULVAC) was used for gas analysis.

3. Results and Discussion

3.1 Decomposition of benzene or toluene in autoclave

Figure 3 shows the decomposition process of benzene on TiO₂ in air as a function of temperature, as monitored by

Fig. 3. Decomposition of benzene in air by ST01 as a function of temperature.

Fig. 4. Decomposition of toluene in air by means of ST01 as a function of temperature.

a mass spectrometer. The amounts of O_2 and CO_2 are expressed relative to the amount of N_2 . Note that benzene starts to decompose even at $200^\circ C$ and completely decomposes at approximately $500^\circ C$, forming CO_2 and H_2O (not shown), whereas no other species were detected except for N_2 and O_2 in air. The CO_2 concentration increases as the decomposition reaction of benzene proceeds, whereas the O_2 concentration decreases because O_2 is used up for the combustion of fragments derived from benzene. The decomposition of toluene is shown in Fig. 4. The process appears similar to that of benzene. However, the decomposition is completed at a lower temperature of about $350^\circ C$ than that of benzene. This is because toluene is a polar molecule due to an electron-donating methyl group. This facilitates the adsorption of toluene on TiO_2 and its subsequent decomposition.

To study the role of oxygen in the decomposition of benzene, a comparison experiment was carried out in N_2 (i.e., in the absence of O_2) under the same conditions. As observed from Fig. 5, benzene remains undecomposed even at $500^\circ C$ and no change in CO_2 concentration is recognized. This points out the importance of the presence of oxygen for decomposition. Then, another reference experiment was also carried out in air, using $\alpha-Al_2O_3$ in place of ST01. Figure 6 shows the decomposition as a function of temperature. Only a slight decomposition of benzene is recognized above $400^\circ C$, accompanied by a decrease and an increase in O_2

Fig. 5. Decomposition of benzene in N_2 by means of ST01 as a function of temperature.

Fig. 6. Decomposition of benzene in air by $\alpha-Al_2O_3$ as a function of temperature.

and CO_2 concentrations, respectively. The above results indicate how powerful ST01 is for decomposition as compared with $\alpha-Al_2O_3$.

3.2 Characterization of intermediates in decomposition of benzene and toluene

The intermediate samples extracted from the reaction vessel during the decomposition (see §2.3) in steps of $50^\circ C$ were characterized by DSC, ESR, Raman spectroscopy, and mass spectrometry.

ST01 is pure white and nonsticky powder. On the other hand, all “benzene/ST01” and “toluene/ST01” powders extracted were brown and highly sticky irrespective of the sampling temperature, although the extent of coloration was different. This clearly indicates that certain interactions took place between the adsorbent (TiO_2) and the adsorbate (benzene or toluene). Figure 7 shows the DSC curves of benzene/ST01 and toluene/ST01, both of which were sampled at $200^\circ C$. The exothermic peaks appear at about 330 and $350^\circ C$ for benzene/ST01 and toluene/ST01, respectively, indicating the decomposition of benzene and toluene in air. The exothermic peak of toluene/ST01 is present at a lower temperature than that of benzene/ST01 by about $20^\circ C$. Furthermore, all intermediates sampled in the range between 100 and $300^\circ C$ show similar DSC curves for both benzene/ST01 and toluene/ST01.

The Raman spectra of the samples used for the above DSC are shown in Fig. 8. In toluene/ST01, a peak shift of about 2 cm^{-1} is observed toward higher wavenumbers. On the other hand, no noticeable peak shift is recognized in benzene/ST01. Nevertheless, the background at higher

Fig. 7. DSC curves of benzene/STO1 and toluene/STO1 powders, both of which were sampled at 200°C.

Fig. 8. Peak shifts of Raman spectra in benzene/STO1 and toluene/STO1 powders sampled at 200°C.

Fig. 9. (a) ESR spectra of benzene/STO1 powders sampled at various temperatures and (b) difference in spectrum as obtained by subtracting the signal of STO1 from that of benzene/STO1 sampled at 200°C.

wavenumbers is enhanced to increase, suggesting the adsorption of benzene on TiO_2 .

As described above, the intermediates (benzene/STO1 and toluene/STO1) were brown, but the extent of coloration varies, depending on the temperature. The brownish color intensified with increasing temperature and was deepest at 200–250°C and then faded out gradually, ending up as white again at 350°C. This color change is well correlated with the appearance and disappearance of ESR signals, as shown below. Since both toluene/STO1 and benzene/STO1 behaved nearly in the same way, only the latter result is shown below. Figure 9(a) shows the ESR spectra of STO1 and benzene/STO1 powders sampled at 200, 250, 300, and 350°C. One can observe a small shoulder (or a small peak) in all benzene/STO1 spectra at about 338.5 mT. This is ascribed to the ESR signal derived from the adsorbed benzene on TiO_2 , as shown by the difference in spectra shown in Fig. 9(b), where the ESR signal of STO1 is subtracted from that of the intermediate at 200°C. The shoulder signal becomes stronger with increasing temperature and becomes maximum at approximately 200–250°C.

Then, it becomes again and disappears at approximately 350°C. The appearance and disappearance of both the ESR signal and the brownish color of the intermediates indicate the formation of the intermediate (benzene/STO1 or toluene/STO1) and its decomposition, respectively. Above 350°C, neither the ESR signal nor the brownish color can be recognized. However, this does not mean that benzene is not decomposed, but this does mean that benzene is immediately decomposed due to the increased number of holes above 350°C.

An important question then arises as to the species formed on TiO_2 in the intermediate state. To analyze this, the mass spectra of the intermediates extracted at 200°C were measured under vacuum at various temperatures. The mass spectra for the fraction collected in the range between 100 and 400°C are found to include only H_2O , CO , and CO_2 , whereas the fragments derived from benzene begin to gradually appear above 400°C. Figure 10 shows the mass spectrum of the fraction collected at 480°C for 30 min. The fragments derived from benzene are clearly recognized at mass numbers of approximately 78, 51, and 39 in addition to

Fig. 10. Mass spectrum of desorbed species of benzene/STO1 powders sampled at 200 °C for fraction collected at 480 °C for 30 min.

Fig. 11. Mass spectrum of desorbed species of benzene/STO1 powders sampled at 350 °C for fraction collected in temperature range of 280–380 °C. The experiment was carried out in a mixture of N₂ and O₂ (ratio: N₂/O₂ = 9/1).

the peaks of H₂O, CO, and CO₂. This clearly indicates that benzene (or only a slightly decomposed benzene) is firmly adsorbed on the surface of TiO₂ and desorbed only above about 400 °C.

3.3 Elementary reaction in decomposition of benzene

As shown in Fig. 5, no decomposition of benzene occurs in N₂. In other words, the presence of oxygen is indispensable for the complete decomposition of benzene. This fact prompted us to believe that we can decelerate the reaction rate under oxygen-deficient conditions with an excess of N₂ so as to identify the intermediates of benzene. This experiment was carried out in a mixture of N₂ and O₂ (ratio: N₂/O₂ = 9/1) and the intermediates were sampled at various temperatures. Among these, the intermediate sampled at 350 °C is found to include decomposition products. Figure 11 shows the mass spectra measured for the fraction collected in the temperature range between 280 and 380 °C. We observed a series of fragments composed of ethylene, butane, propene, and butadiene. These results suggest that benzene is completely decomposed into H₂O and CO₂ via ethylene, butane, propene, and butadiene.

3.4 Decomposition of PM as monitored using Raman, ESR, and DSC spectra

Since the decomposition of PM is supposed to occur at the “solid (PM)/solid (TiO₂)” interface, it is crucial to increase

(a)

(b)

Fig. 12. (a) Peak shifts of Raman spectrum of *E_g* mode at approximately 150 cm⁻¹ and (b) Raman spectra showing two bands due to aromatic rings for sample 1 (i.e., a mixture of PM and STO1) heated in air at various temperatures.

the contact frequency between TiO₂ and PM and also to maintain the contact time as long as possible.

Figure 12(a) shows the Raman spectra of the *E_g* mode for sample 1 (i.e., a mixture of PM and STO1; see §2.4) heated at various temperatures, using STO1 as the reference. Even at room temperature, a small peak shift of about 4 cm⁻¹ toward higher wavenumbers is observed. Then, a reverse peak shift toward lower wavenumbers is recognized when heated at 300 °C and the shift is even more enhanced at 400 °C. Figure 12(b) shows the Raman spectra in the range between 1200 and 1800 cm⁻¹. Two characteristic bands due to aromatic rings appear at approximately 1350 and 1600 cm⁻¹ at room temperature and these bands remain even at 300 °C. Then, these bands disappear completely at 400 °C. In parallel, ESR measurements were also carried out on the following samples as a function of temperature: PM and sample 1. Figures 13(a) and 13(b) show the difference in the spectra of PM species, where the ESR signal of STO1 is subtracted from that of PM or sample 1. No change is recognized in PM up to 100 °C. Then, the signal begins to weaken above 200 °C. On the other hand, in sample 1, we observed a slight reduction in intensity even at 100 °C and then the signal disappears completely at 200 °C. This result clearly indicates that the presence of TiO₂ is, to some extent, effective in decomposing PM. This is further confirmed by a comparison experiment based on CR80 (i.e., inert TiO₂) in place of STO1 that gives no effect. However, the color of

Fig. 13. (a) ESR spectra at various temperatures: (a) PM and (b) sample 1 (i.e., mixture of PM and ST01).

sample 1 (initially gray) is not yet entirely white (ST01), suggesting that the PM decomposition is still incomplete.

Then, sample 2 (i.e., pressed sample of sample 1) was tested, which provides better contacts between PM and ST01 during the decomposition. Figure 14 shows the DSC curves of samples 1 and 2. The shadowed area corresponds to the difference in exothermic energy that amounts to 27.7 J/g. This indicates that the press effect is significant for the PM decomposition. Sample 2, however, is not entirely white after DSC. Therefore, further trial was made to heat sample 1 under a pressure of about 280 N/m² at 350 °C for 5 min ("hot press"). Then, the gray color disappeared completely, indicating that PM was completely decomposed.

The above results suggest that even PM can basically be decomposed into H₂O and CO₂, provided that the contact frequency between PM and TiO₂ is high and that the contact time is sufficiently long while heating.

4. Conclusions

The complete decomposition of benzene, toluene, and

Fig. 14. DSC curves of sample 1 (i.e., a mixture of PM and ST01) and sample 2 (i.e., pressed sample of sample 1).

PM contained in the exhaust of diesel engines has been investigated. The conclusions can be summarized as follows.

1. Strong interactions are found between the adsorbate (benzene or toluene) and the adsorbent (TiO₂) as indicated by the appearance of brownish benzene/ST01 or toluene/ST01 powders that are further associated with the formation of radicals. The present spontaneous adsorption of benzene or toluene on TiO₂ is quite advantageous to their subsequent decomposition into H₂O and CO₂.
2. Benzene or toluene decomposes completely into H₂O and CO₂ at about 350–500 °C. The elementary decomposition of benzene proceeds via ethylene, butane, propene, and butadiene.
3. PM is also found to completely decompose, provided that the contact frequency between PM and TiO₂ is high and that the contact time is sufficiently long while heating.

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