

Complete decomposition of benzene, toluene and particulate matter (PM) contained in the exhaust of diesel engines by means of thermally-excited holes in TiO_2 at high temperatures

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Abstract

Titanium dioxide was once extensively investigated as a photoconductor for the electrophotographic photoreceptor at its incunabula. Nowadays, it has attracted attention as a material for photocatalyzers, solar cells as well as their related areas. We report here another application of titanium dioxide. Our motivation is to make use of thermally-generated holes for decomposition of organic compounds. We have previously reported on a decomposition system of organic wastes by use of thermally-excited holes in TiO_2 at high temperatures (about 350–500 °C). In the present investigation, we aim at applying this technology to complete decomposition of benzene, toluene and particulate matter (PM) contained 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 and ESR spectra 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 pressure of about 280 N/m^2 at about 350 °C.

1. Introduction

We have previously investigated 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 how to dispose used optical disks. Our decomposition system is similar to the photocatalytic one which makes use of photogenerated holes for the oxidation decomposition of a variety of substances. However, ours differs distinctly in the utilization of thermally-excited holes at high temperatures (say, about 350 °C) in combination with a molten state of PC, as shown in Fig.1. A great 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 state [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 $E_g = 3.2$ eV. This number has approximately been confirmed by our previous experiment based upon single crystals of TiO_2 of the rutile phase [3]. In addition, PC melts into liquid at these temperatures to form

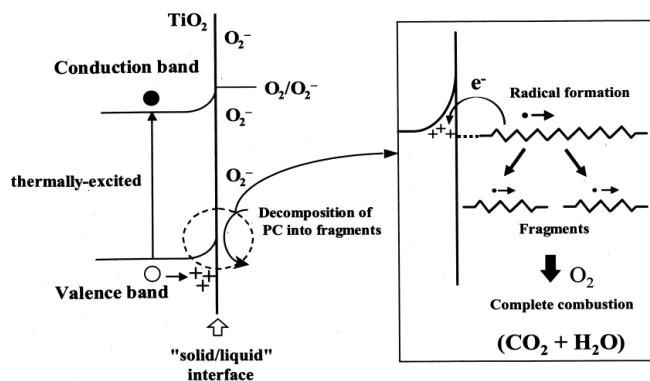


Fig. 1. Decomposition process of PC at the “ TiO_2 /PC” interface by means of thermally-generated holes.

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 as well as thermosetting polymers (*i.e.* three-dimensional polymers which have no melting point) can completely be decomposed [3]. We have also confirmed that any kinds 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 the decomposition has also been clarified to proceed in such a way that the radicals are initially formed in PC by means of 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 PM (particulate matter) included in the exhaust of diesel engines can be decomposed in terms of the present technology. Diesel engines have been widely used for trucks, passenger cars, vessels, heavy machineries, and so on. Diesel engines are characterized by a variety of merits such as high thermal efficiency of about 45–50 % which is higher than in gasoline engines by about 10–15 %, as well as high torque, robust, low fuel consumption etc. On the other hand, the main drawback of diesel engines consists in the exhaust comprising mainly of hydrocarbons (benzene, toluene etc.), PM and NO_x . PM is a carbon-like, black powder comprising aromatic and aliphatic hydrocarbons and sulfates. In the present study, we focus on the complete decomposition of benzene, toluene and PM.

2. Experiment

2.1 Materials

TiO₂ powders of ST01 (anatase form) and CR80 (rutile form) were obtained from Ishihara Sangyo Kaisha (ISK). ST01 is an active TiO₂ and designed for photocatalysts with a specific surface of about 278 m²/g and a grain size of about 7 nm. On the other hand, CR80 is a surface-coated TiO₂ used widely as a white pigment and used as an inert reference in the present investigation together with α -Al₂O₃ (Junsei Chemical Co., Ltd.). All powdered samples were calcinated in air at 500 °C for 1 h before use. Due to these calcinations, the specific surface of ST01 was diminished from 278 to 96 m²/g, but remains nearly unchanged with further calcination. On the other hand, no noticeable change was recognized in CR80 and α -Al₂O₃. Benzene and toluene of the GR grade were purchased from Wako Pure Chemical Industries, Ltd. PM powders were supplied by ISUZU Advanced Engineering Center, Ltd.

2.2 Autoclave used for decomposition of benzene and toluene

An autoclave equipped with a mass spectrometer was specially designed for the present experiment. The schematic representation is given in Fig. 2. The volume of the reaction vessel is 300 ml, in which 40 g of TiO₂, or CR80 or α -Al₂O₃ were charged. The stirrer rotates at a rate of 150 rpm. Gases (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 to 200 ml/min while the temperature was varied in the range between 100 and 500 °C. The emerging gas was sampled at various temperatures and analyzed by mass spectrometer.

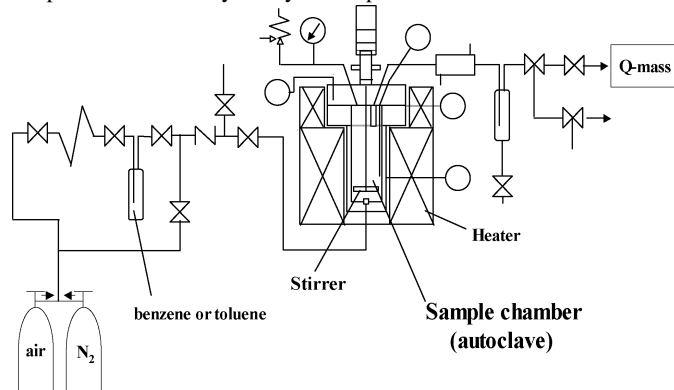


Fig. 2. Schematic representation of the autoclave used for decomposition experiments. Q-mass denotes a quadrupole mass

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

In order to study the intermediates in the decomposition process, ca 100 mg of TiO₂ powders were extracted from the reaction vessel every 50 °C in situ in the temperature range from 100 to 500 °C. These samples were colored brown and highly

viscous due to reactions between adsorbate (benzene or toluene) and adsorbent (TiO₂) as described later in section 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 as prepared by pressing sample 1 with a pressure of 280 N/m². PM/CR80 samples were also prepared as the reference with the same composition.

2.5 Equipment for measurement

A DSC 8230 and a TGA 8120 from RIGAKU were used for measurements of DSC (Differential Scanning Calorimetry) and TGA (Thermogravimetric Analysis), respectively. The heating rate was 10 °C/min in both measurements. Raman spectra were measured by a NRS-3100 laser Raman spectrophotometer from JASCO. Measurements of Electron Spin Resonance (ESR) were carried out with a JES-FA200 from JEOL. ESR signal were corrected by Mn markers and the radical concentrations were estimated on the basis of DPPH (α , α' -diphenyl- β -picrylhydrazyl) 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

Fig. 3 shows the decomposition process of benzene on TiO₂ in air as a function of temperature, as monitored by mass spectrometer. The amount of O₂ and CO₂ is expressed relative to the amount of N₂. It is remarkable to note that benzene starts decomposing even under 200 °C and completely decomposes around 500 °C, giving rise to CO₂ and H₂O (not shown) while no other species were detected except for N₂ and O₂ in air. The CO₂ concentration increases as the decomposition reaction of benzene proceeds; whereas the O₂ concentration decreases, because O₂ is used up for the combustion of fragments derived from benzene. The decomposition process of toluene is shown in Fig. 4. The process looks similar to that of benzene. However, the decomposition is completed at a lower temperature of about 350 °C than that in benzene. This is because toluene is a polar molecule due to an electro-donating methyl group. This facilitates the adsorption of toluene on TiO₂ and its subsequent decomposition.

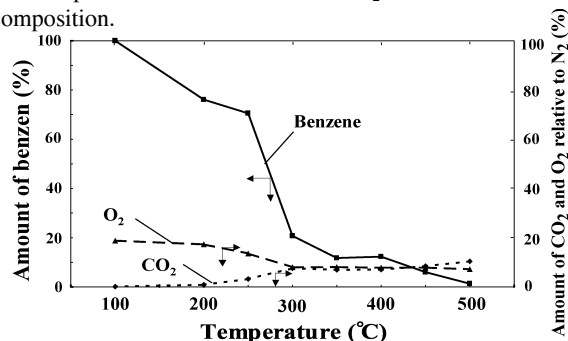


Fig. 3. Decomposition process of benzene in air by means of ST01 as a function of temperature.

In order to study the role of oxygen in the decomposition process of benzene, a comparison experiment was carried out in N_2 (i.e. in the absence of O_2) under the same conditions. As seen from Fig. 5, benzene remains undecomposed even at 500 °C and no change is recognized in CO_2 concentration. 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. Fig. 5 shows again the decomposition process using $\alpha-Al_2O_3$ as a function of temperature. Only a slight decomposition of benzene is recognized above 400 °C, accompanied by the decrease and increase of O_2 and CO_2 , respectively. The above results indicate how ST01 is powerful for decomposition as compared with $\alpha-Al_2O_3$.

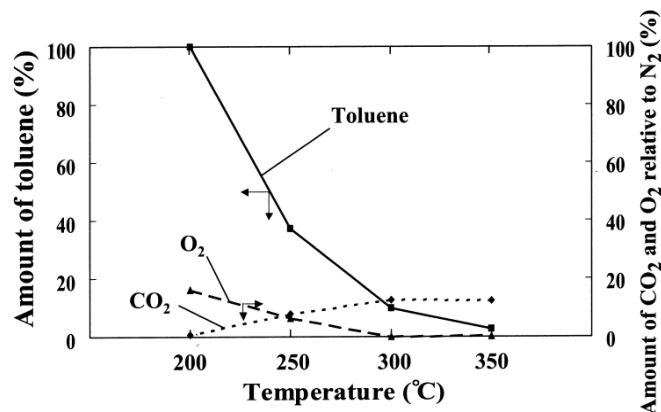


Fig. 4. Decomposition process of toluene in air by means of ST01 as a function of temperature.

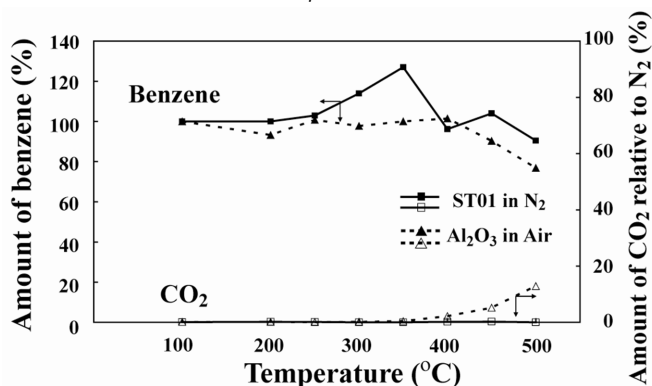


Fig. 5. Decomposition processes of benzene in N_2 by means of ST01 and in air by means of $\alpha-Al_2O_3$ as a function of temperature.

3.2 Characterization of the intermediates in the decomposition process of benzene and toluene

The intermediate samples extracted from the reaction vessel during the decomposition process (see section 2.3) in steps of 50 °C were characterized by DSC, ESR, Raman and mass spectra.

ST01 is pure white and non-sticky powders. On the other hand, all "benzene/ST01" and "toluene/ST01" powders extracted were colored 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 adsorbent (TiO_2) and adsorbate (benzene or toluene). Fig. 6 shows the DSC curved for benzene/ST01 and toluene/ST01, both of which were sampled at 200 °C. The exothermic peaks appear

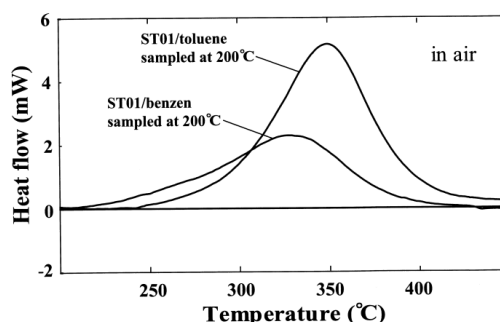


Fig. 6. DSC curves of benzene/ST01 and toluene/ST01 powders, both of which were sampled at 200 °C.

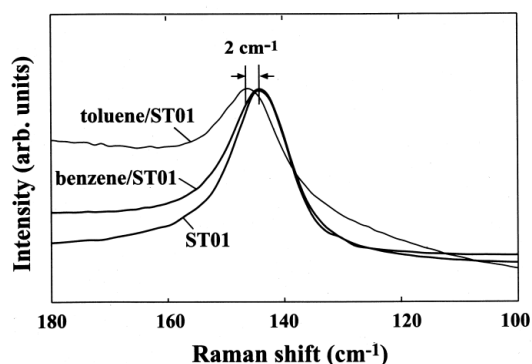


Fig. 7. Peak-shifts of the Raman spectra in benzene/ST01 and toluene/ST01 powders sampled at 200 °C.

at about 330 and 350 °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 °C. Furthermore, all intermediates sampled in the range between 100 and 300 °C shows similar DSC curves for both benzene/ST01 and toluene/ST01.

The Raman spectra of the samples used for the above DSC measurements are shown in Fig. 7. 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 wavenumbers is observed to increase, suggesting the adsorption of benzene on TiO_2 .

As described above, the intermediates (benzene/ST01 and toluene/ST01) were colored brown, but the extent of coloration varies, depending on the temperature. The brownish color was more intensified with increasing temperature and was deepest at 200-250 °C and then faded out gradually, ending up with white again at 350 °C. The present color change is well correlated with the appearance and disappearance of ESR signals, as shown below. Since both toluene/ST01 and benzene/ST01 behaved nearly in the same way, only the latter result is shown below. Fig. 8(a) shows the ESR spectra for ST01 as well as benzene/ST01 powders sampled at 200, 250, 300 and 350 °C. One can see a small shoulder (or a small peak) in all benzene/ST01 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 spectra given in Fig. 8(b), where the ESR signal of ST01 is subtracted from that of the intermediate at 200 °C. The shoulder signal grows up with increasing temperature and becomes maximum around

200–250 °C. Then, it decreases again and disappears around 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/ST01 and toluene/ST01) and its decomposition, respectively. Above 350 °C, neither ESR signal nor 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 TiO₂ in the intermediate state. To analyze this, 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 H₂O, CO and CO₂; whereas the fragments derived from benzene begin to gradually appear above 400 °C. Fig. 9 shows the mass spectrum for the fraction collected at 480 °C for 30 min. The fragments derived from benzene are clearly recognized around mass numbers of 78, 51 and 39 in addition to the peaks of H₂O, CO and CO₂. This clearly indicates that benzene (or only slightly decomposed benzene) is firmly adsorbed on the surface of TiO₂ and desorbed only above about 400 °C.

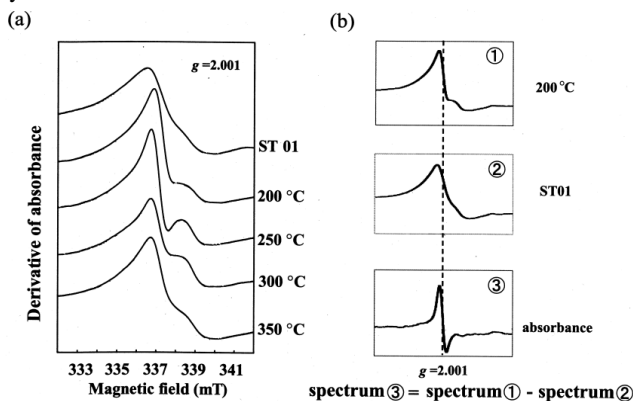


Fig. 8. (a) ESR spectra of the benzene/ST01 powders sampled at various temperatures and (b) difference spectrum as obtained by subtracting the signal of ST01 from that of benzene/ST01

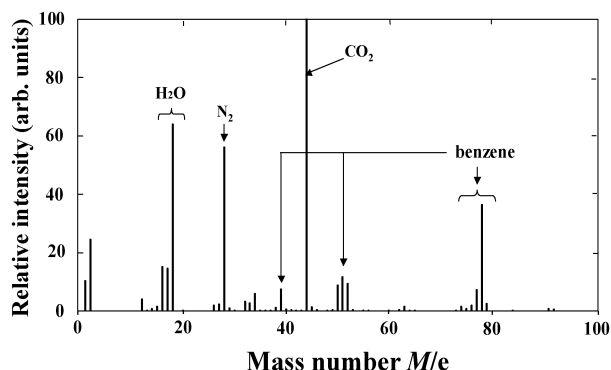


Fig. 9. Mass spectrum of desorbed species of the benzene/ST01 powders sampled at 200 °C for the fraction collected at 480 °C for 30 min.

3.3 Elementary reaction in the decomposition process of benzene

As shown in Fig. 5, no decomposition of benzene occurs in N₂. In other words, the presence of oxygen is indispensable for complete decomposition of benzene. This fact prompted us to believe that we can de-accelerate 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. Fig. 10 shows the mass spectra measured for the fraction collected in the temperature range between 280 and 380 °C. There 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.

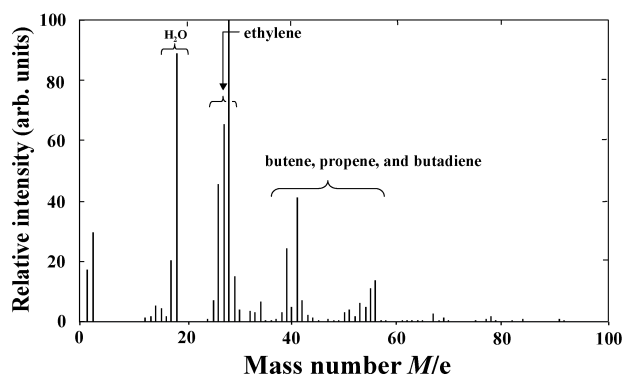


Fig. 10. Mass spectrum of the desorbed species of the benzene/ST01 powders sampled at 350 °C for the fraction collected in the temperature range of 280–380 °C. The experiment was carried out in a mixture of N₂ and O₂ (ratio: N₂/O₂=9/1).

3.4 Decomposition of PM as monitored by 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 the contact frequency between TiO₂ and PM and also to keep the contact time as long as possible.

Fig. 11(a) shows the Raman spectra of the *E_g* mode for sample 1 (*i.e.* mixture of PM and ST01: see section 2.4) heated at various temperatures, using ST01 as the reference. Even at room temperature, a small peak-shift of about 4 cm⁻¹ toward higher wavenumbers is observed. Then, the reverse peak-shift toward lower wavenumbers is recognized when heated at 300 °C and the shift is even more enhanced at 400 °C. Fig. 11(b) shows the Raman spectra in the range between 1200 and 1800 cm⁻¹. Two characteristic bands due to aromatic rings appear around 1350 and 1600 cm⁻¹ at room temperature and these 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. Figs. 12(a) and 12(b) show the difference spectra for PM species, where the ESR signal of ST01 is subtracted from that of PM or sample 1. No change is recognized in PM up to 100 °C. Then, the signal begins to reduce above 200 °C. On the other hand, in sample 1, there

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. In fact, this is further confirmed by a comparison experiment based upon CR80 (*i.e.* inert TiO₂) in place of ST01 that gives no effect. However, the color of 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 process. Fig. 13 shows the DSC curves for samples 1 and 2. The shadowed area corresponds to the difference in exothermic energy, which amounts to 27.7 J/g. This indicates that the press effect is significant for the PM decomposition. The color of sample 2 exhibits, however, not entirely white after DSC measurements. Therefore, a further trial was made to heat sample 1 under 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 the even PM can basically be decomposed into H₂O and CO₂, provided that the contact frequency between PM and TiO₂ is high and the contact time is sufficiently long while heating.

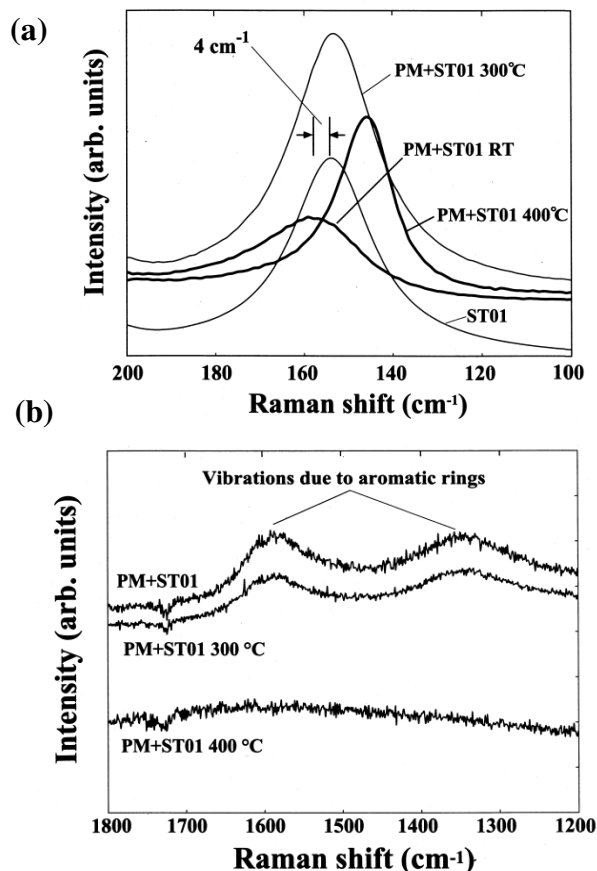


Fig. 11. (a) Peak-shifts of the Raman spectrum of the E_g mode around 150 cm⁻¹ and (b) Raman spectra showing two bands due to aromatic rings for sample 1 (*i.e.* mixture of PM and ST01) heated in air at various temperatures.

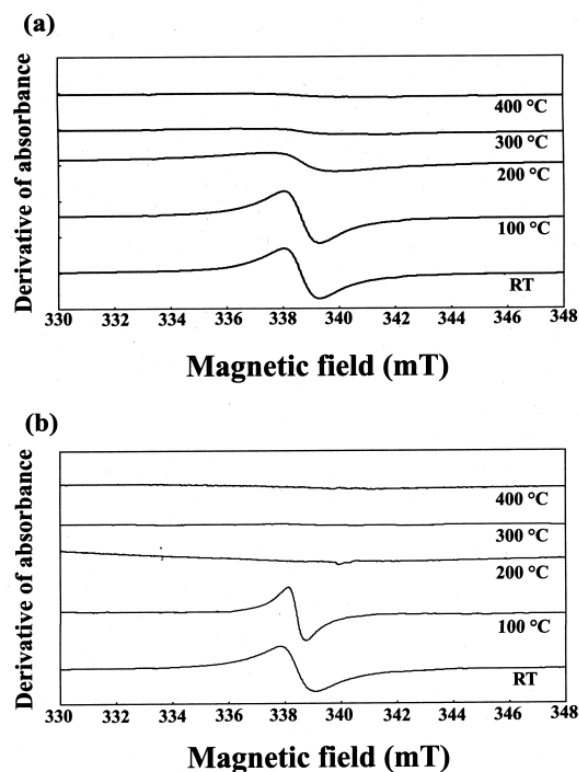


Fig. 12 (a) ESR spectra at various temperatures: (a) PM and (b) sample 1 (*i.e.* mixture of PM and ST01).

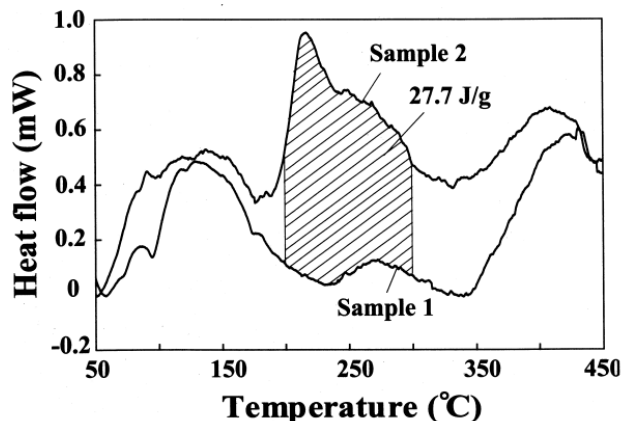


Fig. 13 DSC curves of sample 1 (*i.e.* mixture of PM and ST01) and sample 2 (*i.e.* pressed sample of sample 1).

4. Conclusions

Complete decomposition of benzene, toluene and PM contained in the exhaust of diesel engines has been investigated. The conclusions can be summarized as follows.

Strong interactions are found between adsorbate (benzene or toluene) and adsorbent (TiO_2) as indicated by the appearance of the brownish color of benzene/ST01 or toluene/ST01 powders that are further associated with the formation of radicals.

The present spontaneous adsorption of benzene or toluene on TiO_2 is quite advantageous to their subsequent decomposition into H_2O and CO_2 . Benzene or toluene decomposes completely into H_2O and CO_2 at about 350–500 °C.

The elementary decomposition-process of benzene proceeds *via* ethylene, butane, propene, and butadiene. PM is also found to completely decompose, provided that the contact frequency between PM and TiO_2 is high and the contact time is sufficiently long while heating.

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