Fixation of TiO$_2$ or SnO$_2$ onto Al$_2$O$_3$ Balls and Its Use as a Compact System for Decomposition of Volatile Organic Compounds

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**Abstract**

Complete decomposition of organic wastes using thermally-generated holes in titanium dioxide at high temperatures has been investigated. In view of the practical use of the present systems, fixation of TiO$_2$ particles on substrates seems to be the core technology. To realize this, we have investigated direct oxidation of Ti or Sn-coated Al$_2$O$_3$ balls in order to prepare thin layers of TiO$_2$ or SnO$_2$ on the Al$_2$O$_3$ surface, respectively. Formation of TiO$_2$ of the rutile phase or SnO$_2$ has been identified by Raman spectra. In addition, complete decomposition of toluene (as an example of volatile organic compounds) has also been confirmed by the TiO$_2$ or SnO$_2$-coated Al$_2$O$_3$ balls at about 500°C.

**Introduction**

Removal of volatile organic compounds (VOC) is one of the most urgent environmental issues at present. For this reason, a compact, inexpensive system with high performance is in great demand. We have previously reported a novel decomposition system of organic wastes (mainly thermoplastic and thermostetting polymers) as well as the exhaust of diesel engines, using a great number of holes generated at about 350–500°C in TiO$_2$ (Mizuguchi, 2001; Mizuguchi and Shinbara, 2004; Shinbara et al., 2005; Makino et al., 2007; and Matsumoto et al., 2008a). Our system is characterized by the use of thermally excited holes at high temperatures (e.g., about 350–500°C) in combination with a molten state of thermoplastics, for example, polycarbonate (PC) as shown in Figure 1.

**Figure 1** A great deal of charge carriers is available in TiO$_2$ at high temperature as shown by the product of the Fermi–Dirac distribution function and the density of states (Kittel, 1986). The number of carriers at room temperature (RT) and 350°C [$n_{RT} = n_0 \exp[-E_g/2kT_{RT}]$ and $n_{350K} = n_0 \exp[-E_g/2kT_{350K}]$, respectively] gives a ratio of $n_{350K}/n_{RT} \approx 8.8 \times 10^5$, where $E_g$ = 3.2 eV. In fact, this number has approximately been confirmed in our previous experiment based on single crystals of TiO$_2$ of the rutile phase (Shinbara et al., 2005). This suggests that any semiconductor can basically be used for the present system, provided that it is stable at high temperature in an oxygen atmosphere. Therefore, oxide semiconductors such as SnO$_2$, ZnO, Cr$_2$O$_3$, etc. come into consideration.

The initial process of the PC decomposition is the capture of bonded electrons to form radicals by thermally generated holes, followed by their propagation throughout the polymer chain to break PC into fragments, resulting in their complete decomposition into H$_2$O and CO$_2$ under oxygen-sufficient conditions (Shinbara et al., 2005). Quite recently, we have also reported that hydrogen is efficiently produced from methanol or methane under oxygen-deficient conditions (Matsumoto et al., 2008b).

**In our previously studies, we worked with powdered TiO$_2$ in an autoclave based upon the fluidized bed system. However, the powder system is obviously not adequate for practical applications, especially for the decomposition of VOCs. Therefore, an attempt has been made in the present investigation to fix TiO$_2$ or related oxides on a substrate. Then, we came across Ti or Sn-coated alumina balls called powder impact plating (PIP) manufactured by Fuji Kihan Co., Ltd. (Miyasaka, 2003). The metal or partly oxidized metal layers are prepared on the surface of Al$_2$O$_3$ balls (about 4 mm in diameter) to a thickness of 1–3 μm by impacting Ti particles (about 2 mm in diameter) with a high speed of about 100–200 m/s for about one hour. This binder-less process is called wide peening cleaning (WPC) or wonder process craft or fine particle bombarding (FPB) process, and is widely used as a surface treatment which suppresses the surface wear of metal tools (Yonekura et al., 2001). Then, we arrived at the idea that we could easily prepare oxide layers of Ti or Sn on Al$_2$O$_3$ balls by directly oxidizing Ti or Sn-coated Al$_2$O$_3$ balls. Since the thermal expansion coefficient of TiO$_2$ or SnO$_2$ is very close to that of Al$_2$O$_3$, the upper-TiO$_2$ or SnO$_2$ layer can never be peeled off from the Al$_2$O$_3$ substrate in our thermal cycles between room temperature and 500°C. An additional merit of using TiO$_2$ or SnO$_2$-coated Al$_2$O$_3$ balls is that the spherical balls can be packed in a glass column in a fashion “close-packed structure” (occupancy: 74%) so that the 26% vacant space is always available for the flow of VOC.

The purpose of the present study is to prepare TiO$_2$ or SnO$_2$-coated Al$_2$O$_3$ balls by oxidation and to evaluate their decomposition ability of toluene known as a typical VOC.

**2. Results and Discussion**

**2.1 Oxidation of Ti or Sn-coated Al$_2$O$_3$-balls**

Ti or Sn-coated Al$_2$O$_3$ balls of about 4 mm in diameter prepared by WPC process were obtained from Fuji Kihan, Co. Ltd. The thickness of the metal layer amounts to 1–3 μm. The Ti or Sn-coated balls display a dark, metallic color. Then, Ti or Sn-coated Al$_2$O$_3$ balls were oxidized in air for one hour at 800°C to give a pure white color as characterized by TiO$_2$/Al$_2$O$_3$ or SnO$_2$/Al$_2$O$_3$.

**Figure 2** shows the Raman spectra for Ti-coated Al$_2$O$_3$ balls before and after oxidation at 800°C, measured by means of a NRS-3100 laser Raman spectrophotometer from JASCO Corp. The Raman spectrum of powdered TiO$_2$ of the rutile phase is...
also shown as the reference. No oxide layer was observed for the Ti-coated Al$_2$O$_3$ balls before oxidation. Similarly, no formation of oxides was recognized either for oxidation at 500°C (not shown here). On the other hand, the typical Raman peaks for the rutile phase (around 240, 445, and 610 cm$^{-1}$) appeared as a result of oxidation at 800°C, and these are in good agreement with those of powdered TiO$_2$ (Balanchandran et al., 1982). It is also important to note that the two peaks at about 3500 cm$^{-1}$ are attributed to Al$_2$O$_3$, since these are only observed in Al$_2$O$_3$ before WPC coating. This indicates that the Al$_2$O$_3$ balls are not entirely covered with a Ti-layer, as also shown by our electrical measurements at various points of the Ti-coated surface. This is also the case in Sn-coated Al$_2$O$_3$ balls.

**Fig. 2** Raman spectra for Ti-coated alumina balls before and after oxidation

Likewise, Sn-coated Al$_2$O$_3$ balls were oxidized at 800°C. **Figure 3** shows the Raman spectra before and after oxidation in air at 800°C, where the spectrum for powdered SnO$_2$ is also shown as the reference. No characteristic peaks for SnO$_2$ were observed (except for the one around 418 cm$^{-1}$) for the Sn-coated Al$_2$O$_3$ balls before oxidation. Then, the oxidation at 800°C yields the Raman peaks, which include some typical peaks of SnO$_2$ (378, 418, 580 and 635 cm$^{-1}$). However, the peak intensity is considerably weak. The cause can presumably be attributed to the fact that the Sn-layer prepared on Al$_2$O$_3$ balls is too thin to give characteristic Raman peaks with proper intensities.

**Fig. 3** Raman spectra for Sn-coated alumina balls before and after oxidation

### 2.2 Decomposition of toluene in a glass column containing TiO$_2$ or SnO$_2$/Al$_2$O$_3$ balls

Decomposition of toluene was carried out in a Pyrex® glass column (28 mm in diameter), which contains TiO$_2$/Al$_2$O$_3$ balls (150 mm long) as shown in **Figure 4**. The column was heated by an external furnace at a heating rate of about 15°C/min. O$_2$ was bubbled into toluene to prepare saturated vapor of toluene (2.28 vol%). The gas flow rate was 50 mL/min. Gas analysis was made by a quadrupole mass spectrometer (Q-Mass model: RG-102 from ULVAC, Inc.) as a function of temperature.

**Fig. 4** Column with TiO$_2$-coated Al$_2$O$_3$ balls

**Fig. 5** Decomposition of toluene by TiO$_2$/Al$_2$O$_3$ balls as a function of temperature; the CO$_2$ quantity is expressed as the percent ratio of the partial pressure of CO$_2$ to the total pressure

**Figure 5** shows the decomposition of toluene as a function of temperature. The decomposition of toluene starts around 300°C and is almost completed at 500°C. At the same time, the amount of CO$_2$ increases remarkably, suggesting that toluene is completely decomposed into H$_2$O and CO$_2$. In fact, no other species other than these gases were detected according to the mass spectrometer. This is a good result. However, as compared with our previous system based upon a fluidized bed system (Makino et al., 2007), the onset temperature of decomposition and the temperature of complete decomposition are still higher. That is, the onset and complete temperatures are 200 and 350°C, respectively, in a fluidized bed system with a gas flow rate of 200 mL/min. It should be noted, however, that our fluidized bed system using optimized TiO$_2$ powders is the most efficient system at the moment, while our goal in the present investigation is to develop a simple, inexpensive system on the basis of the TiO$_2$/Al$_2$O$_3$ balls. The experiment below with SnO$_2$/Al$_2$O$_3$ balls gives a more encouraging result.

**Figure 6** illustrates the decomposition of toluene on the basis of SnO$_2$/Al$_2$O$_3$ balls in lieu of TiO$_2$/Al$_2$O$_3$. The decomposition proceeds more rapidly than that with TiO$_2$/Al$_2$O$_3$, and is almost equivalent to that of our fluidized bed system, although the gas flow rate is one-fourth and the decomposition temperature is
still higher by about 100°C as compared with the fluidized bed system (Makino et al., 2007).

A reference experiment was also carried out using Al2O3-balls alone (α-phase) in stead of TiO2/Al2O3 balls, and the result is shown in Figure 7. The decomposition starts at about 350°C and the decomposition is still incomplete at 500°C. Nevertheless, the Al2O3-balls are found to work as an oxide semiconductor and are effective for the decomposition of toluene.

Conclusions

Direct oxidation of Ti or Sn-coated alumina balls has been carried out in air at 800°C. The TiO2 or SnO2-layer thus formed is quite stable and remains firmly on Al2O3 balls, even for thermal cycles between room temperature and 500°C. The column system with TiO2 or SnO2-coated Al2O3 balls is found to be effective in completely decomposing toluene. The present system is quite simple and thus appropriate for continuous operation for the removal of dilute VOC gases in air.

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Literature Cited


