Fixation of TiO₂ or SnO₂ onto Al₂O₃ Balls
and Its Use as a Compact System for Decomposition of
Volatile Organic Compounds

Daigo YAMAGUCHI, Shigeru SUZUKI, and Jin MIZUGUCHI

Department of Applied Physics, Graduate School of
Engineering, Yokohama National University
79-5 Tokiwadai, Hodogaya-ku, 240-8501 Yokohama, Japan
E-mail: mizu-j@ynu.ac.jp

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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 TiO₂ particles on substrates seems to be the core technology. To realize this, we have investigated direct oxidation of Ti or Sn-coated Al₂O₃ balls in order to prepare thin layers of TiO₂ or SnO₂ on the Al₂O₃ surface, respectively. Formation of TiO₂ of the rutile phase or SnO₂ 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 TiO₂ or SnO₂-coated Al₂O₃ 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 thermosetting polymers) as well as the exhaust of diesel engines, using a great number of holes generated at about 350–500°C in TiO₂ (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**. A great deal of charge carriers is available in TiO₂ 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 $n_{623K} = n_0 \exp[-E_g/2kT_{623K}]$, respectively] gives a ratio of $n_{623K}/n_{RT} \approx 8.8 \times 10^{13}$, where $E_g = 3.2$ eV. In fact, this number has approximately been confirmed in our previous experiment based on single crystals of TiO₂ 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 SnO₂, ZnO, Cr₂O₃, 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 H₂O and CO₂ 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).

Fig. 1 Decomposition process of polycarbonate (PC) by means of thermally generated holes in TiO₂

In our previously studies, we worked with powdered TiO₂ 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 TiO₂ 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 Al₂O₃ 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 Al₂O₃ balls by directly oxidizing Ti or Sn-coated Al₂O₃ balls. Since the thermal expansion coefficient of TiO₂ or SnO₂ is very close to that of Al₂O₃, the upper-TiO₂ or SnO₂ layer can never be peeled off from the Al₂O₃ substrate in our thermal cycles between room temperature and 500°C. An additional merit of using TiO₂ or SnO₂-coated Al₂O₃ 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 TiO₂ or SnO₂-coated Al₂O₃ 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 Al₂O₃-balls

Ti or Sn-coated Al₂O₃ 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 Al₂O₃ balls were oxidized in air for one hour at 800°C to give a pure white color as characterized by TiO₂/Al₂O₃ or SnO₂/Al₂O₃.

Figure 2 shows the Raman spectra for Ti-coated Al₂O₃ 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 TiO₂ of the rutile phase is

also shown as the reference. No oxide layer was observed for the Ti-coated Al_2O_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 (Balachandran *et al.*, 1982). It is also important to note that the two peaks at about 3500 cm^{-1} are attributed to Al_2O_3 , since these are only observed in Al_2O_3 before WPC coating. This indicates that the Al_2O_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_2O_3 balls.

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

Likewise, Sn-coated Al_2O_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_2O_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_2O_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 $\text{SnO}_2/\text{Al}_2\text{O}_3$ balls

Decomposition of toluene was carried out in a Pyrex® glass column (28 mm in diameter), which contains $\text{TiO}_2/\text{Al}_2\text{O}_3$ 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_2O_3 balls

Fig. 5 Decomposition of toluene by $\text{TiO}_2/\text{Al}_2\text{O}_3$ 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_2O 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 $\text{TiO}_2/\text{Al}_2\text{O}_3$ balls. The experiment below with $\text{SnO}_2/\text{Al}_2\text{O}_3$ balls gives a more encouraging result.

Figure 6 illustrates the decomposition of toluene on the basis of $\text{SnO}_2/\text{Al}_2\text{O}_3$ balls in lieu of $\text{TiO}_2/\text{Al}_2\text{O}_3$. The decomposition proceeds more rapidly than that with $\text{TiO}_2/\text{Al}_2\text{O}_3$, 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.

Fig. 6 Decomposition of toluene by SnO₂/Al₂O₃ balls as a function of temperature

Fig. 7 Decomposition of toluene by Al₂O₃ balls alone as a function of temperature

The above results indicate that TiO₂ or SnO₂-coated Al₂O₃ balls are quite effective in completely decomposing toluene. As judged from the temperature of the onset and complete decomposition of toluene as well as the gas flow rate, the decomposition ability in the present system is roughly one-tenth of our previous one based on the fluidized bed system with optimized powdered TiO₂ (Makino *et al.*, 2007). However, the present ball-system is quite simple and thus appropriate for continuous operation for the removal of dilute VOC gases in air.

Finally, it is very important to note that the catalyst (TiO₂ or SnO₂ prepared on Al₂O₃) can be reused without any deterioration in decomposition ability. As described in our previous paper (Matsumoto *et al.*, 2008a), TiO₂ or SnO₂-coated TiO₂ bears a faint brown color upon adsorption of toluene on TiO₂ or SnO₂, followed by complete disappearance of the color as soon as the decomposition is complete.

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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