Preparation of TiO_2 on Ti-wires, or Fixation of Powdered TiO_2 onto Wires of Heating Element for Decomposition of Organic Wastes by Thermally-generated Holes at High Temperatures in TiO_2

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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. We are so far involved in complete decomposition of organic wastes in air by thermally-generated holes in titanium dioxide of the powdered form. In view of the practical use of the present system, fixation of TiO_2 *powders onto a support in the form of, for example, a honeycomb seems to be the core technology. To realize this, we have tried in the present investigation to coat heating elements (Ti, Ni-Cr etc.) with* TiO_2 *powders by means of electrophoretic deposition, or to directly oxidize Ti-coated alumina ball by wet hydrogen at 980 ℃. Both methods are found to be effective. Then, we have carried out decomposition experiments, with the* TiO_2*-coated wires or balls, of polycarbonate as well as benzene and toluene. We have confirmed that these compounds have completely been decomposed into* H_2O *and* CO_2 *by means of thermally-generated holes.*

1. Introduction

We are involved in complete decomposition of organic wastes in air by thermally-generated holes in titanium dioxide of the powdered form (Fig. 1) [1-3]. We have shown that any kinds of polymers as well as VOC (volatile organic compound) can be completely decomposed with our system.

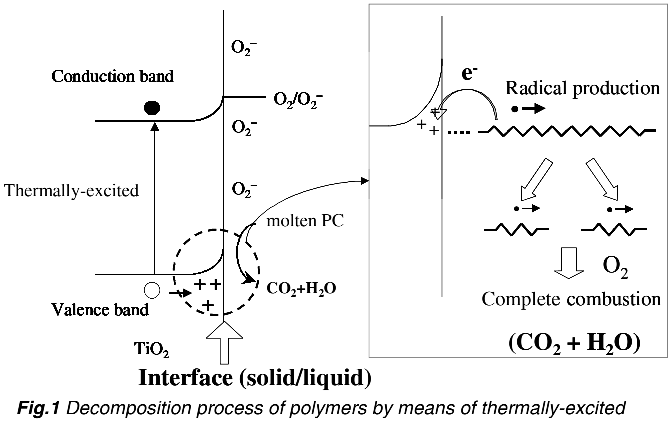

Fig.1 *Decomposition process of polymers by means of thermally-excited holes in* TiO_2*.*

However, our system with powders is not appropriate for practical applications, especially for the removal of gaseous compounds such as VOC. It is, therefore, absolutely necessary to fix TiO_2 powders onto substrates to easily handle our system. We focus in the present investigation on the following two methods. One is to fix powdered TiO_2 onto Ti or Ni-Cr wires by means of electrophoretic deposition. Electrophoretic deposition of powdered substances is a technology similar to electroplating. Ti or Ni-Cr wires serve as the electrodeposition and later as the heating element for the decomposition system. In this way, we can fabricate a built-in heating-system which requires no external furnace. Another advantage of the present system is to fix any powdered TiO_2 without disturbing their characteristics. However, it is necessary to insert a buffer layer (*e.g.* oxides) between metal and TiO_2 in order to adjust the thermal expansion coefficient to avoid peeling-off of the deposit from the core metal. In the present experiment, a thin layer of TiO_2 or Ni-Cr_2O_3 was prepared by anodic oxidation and used as a buffer layer.

The other method is to directly oxidize metal wires or metal-coated alumina balls. We employed here an oxidizing method by means of wet hydrogen which operates at about 980 °C. This enables us first to clean the metal surface by reducing agent of H_2 and then oxidize the metal by oxygen released from water decomposition at about 980 °C. In this way, we can prepare an oxide layer of high quality. In the present experiment, Ti or Sn-coated alumina balls (about 4 mm in diameter) are used because there is no significant difference in thermal expansion coefficient between metal oxides (TiO_2 and SnO_2) and core alumina.

Our goal is to fix TiO_2 layers on substrates and also to evaluate the decomposition ability using polycarbonate (PC) as the reference.

2. Experiment

2.1 Materials

Ti-wires of 0.5 mm in diameter (purity: 99.5 %) were purchased from the NILACO Corporation. Ti or Sn-coated alumina balls of 4 mm in diameter prepared by "Powder Impact Plating" method were obtained from Fuji Kihan, CO. LTD. The thickness of the metal layer amounts to 1-3 µm.

Commercial TiO_2 powders of ST-01 were obtained from Isihara Sangyo Kaisha, Ltd. This is of the anatase form with a specific surface of 298 m^2/g (*ca.* 7 nm in average diameter).

Acetone of the GR grade and sulfuric acid of the GR grade were purchased from Junsei Chemical Co., Ltd and 15 %TMAH solution was obtained from Wako Pure Chemical Industries. Nitrocellulose of RS-60 was obtained from KCNC Ltd. Ni-Cr wire (0.5ϕ) was obtained from NILACO.

Polycarbonate (AD-5503: Mw=18000) was purchased from Teijin Chemicals LTD. Toluene of the GR grade was obtained from Wako Pure Chemicals.

2.2 Suspension for the electrophoretic deposition

Prior to the electrophoretic deposition of powdered TiO_2, a thin oxide buffer-layer of about 1-3 μm was prepared by anodic oxidation on Ti or Ni-Cr wires. 30 % of sulfuric acid was used as the electrolyte. Anodic oxidation was carried out with a current density of about 1.3 A/dm^2 for 30 s.

10 g of ST-01 was suspended in 100 ml of an acetone solution containing 0.12 g of nitrocellulose. The suspension was conditioned in the presence of zirconia balls by a paint shaker for 30 min. Then, 50 ml of this suspension was placed into the electrolytic cell, and 12 μl of TMAH and 4.0 μl of sulfuric acid were added.

Fig. 2 illustrates schematically the experimental setup for electrophoretic deposition. Deposition was carried out in a 50 ml beaker whose diameter was about 45 mm by applying a DC voltage. The heating element (Ti or Ni-Cr wire with buffer layers) works as the anode while a cylindrical Al was used as the counter electrode. The applied voltage was between 3.0 and 500 V and the deposition time was varied from 0.01 to 1 s. After deposition, the wire with deposit was dried.

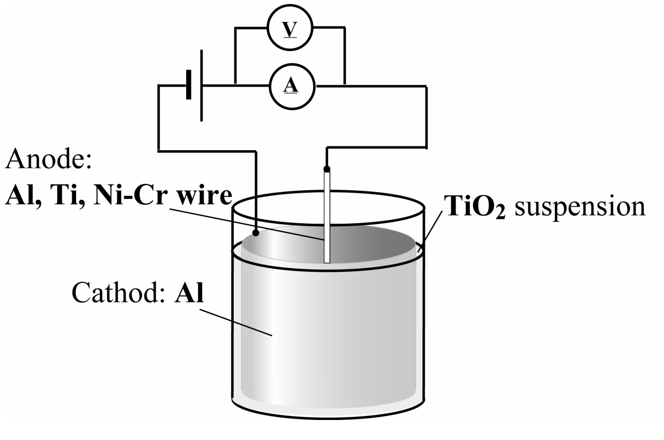

Fig.2 *Experimental setup for electrophoretic deposition.*

2.3 Oxidation by means of wet hydrogen

Fig. 3 shows the schematic illustration of the equipment for oxidation by wet hydrogen. H_2 gas was bubbled through water, and then wet hydrogen was introduced into the furnace. First, the surface of Ti or Ni-Cr wires, or Ti or Sn-balls was cleaned by reducing agent of H_2. Then, oxidation was carried out for 45 min by oxygen released from water decomposition at about 980 °C. The oxide layer amounts to about 3-5 μm.

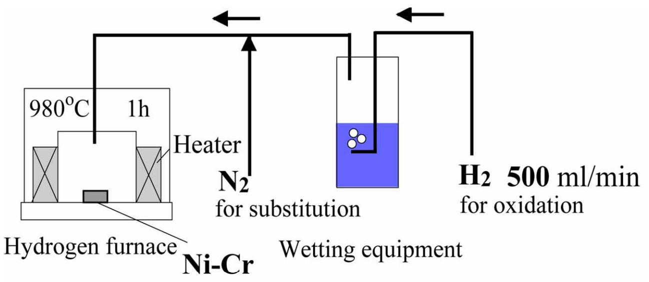

Fig.3 *Experimental setup for the oxidation by means of wet hydrogen.*

3. Results and discussion

3.1 Fixation of powdered TiO_2 onto Ti or Ni-Cr wires

- Anodic oxidation, or oxidation by means of wet hydrogen

Oxide layers as prepared by anodic oxidation or wet hydrogen work excellently as the buffer layer to adjust the thermal expansion coefficient between substrate and TiO_2. The TiO_2 layer deposited on the buffer/metal substrate was never peeled off from the substrate during the heat cycles between room temperature and 500 °C.

- Electrophoretic deposition

Fig. 4 shows the thickness or amount of deposit as a function of applied voltage, where an Al electrode was used as the anode. The amount of deposit increases with deposition time as well as with increasing voltage. For the deposition of about 3 μm in thickness can be achieved at 50 V for 0.01 s.

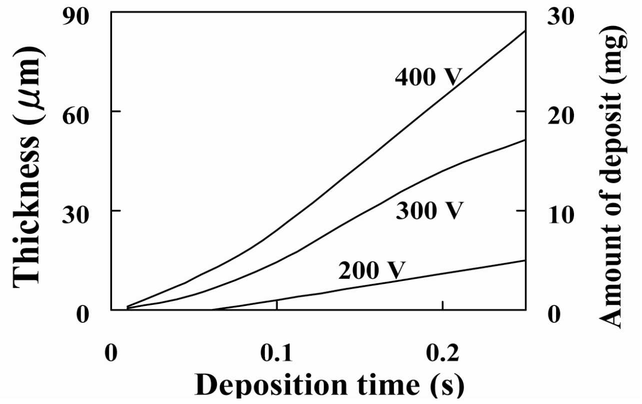

Fig.4 *Thickness or amount of deposit vs deposition time.*

- *Characterization of TiO_2 layers by Raman*

Fig. 5 shows the Raman spectra for TiO_2 powders before and after deposition, both of which are typical of the anatase form. This clearly indicates that ST-01 powders were fixed on wires without disturbing their characteristics.

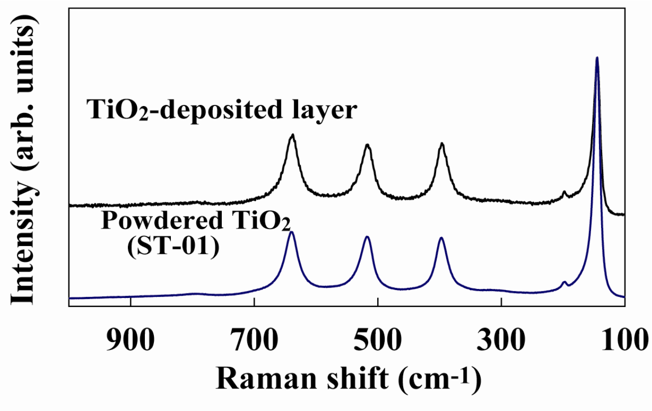

Fig.5 *Raman spectra for electrophoretically-deposited TiO_2 layers on the Ni-Cr_2O_3 layer.*

- *Evaluation of the decomposition ability*

The oxide layer was scraped off from the TiO_2/Ti-wires and then coated with PC as follows. 20 mg of PC was dissolved in 200 ml of toluene at 110 °C. Then, a suspension was prepared composed of 10 mg of powdered TiO_2 and 10 ml of the above solution. PC-coated TiO_2 was then filtered and dried in air.

Fig. 6 shows the DSC curve for PC-coated TiO_2. A broad exothermic peak is observed in the temperature range of 280-480 ºC that corresponds to the decomposition of PC [2-3]. The exothermic energy amounts to 3.215 kJ/g. This is almost equivalent to the released energy in powdered TiO_2 of ST-01 mixed with powdered PC, indicating that that a high decomposition ability of powdered ST-01 is kept even in the electrophoretically deposited films.

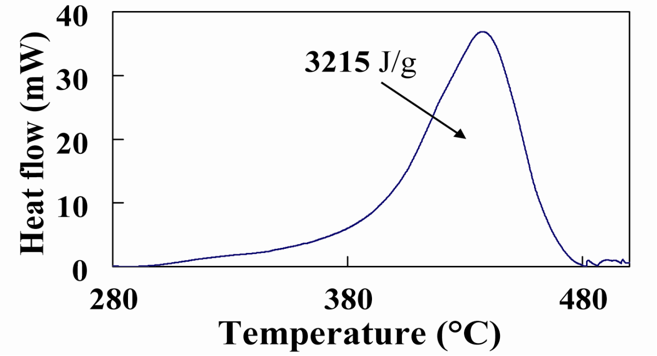

Fig.6 *DSC curve for PC-coated TiO_2.*

Another verification of PC decomposition is shown in Fig. 7 which shows the Raman spectra for PC-coated TiO_2 layers before and after heating at 500 °C for 5 min. The layer before heating is composed of a broad band due to PC and characteristic peaks of the anatase form. However, the broad peak assigned to PC disappears completely after heating, indicating that PC is totally decomposed.

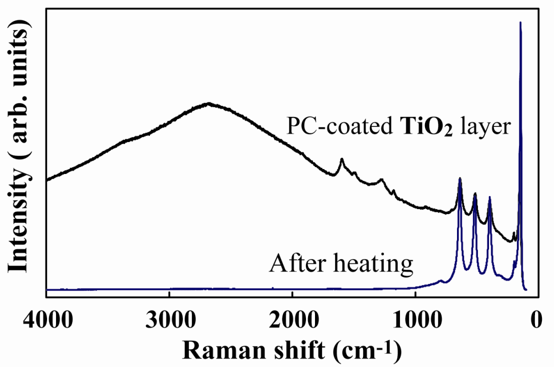

Fig.7 *Raman spectra of PC-coated TiO_2 before and after heating.*

3.2 Fixation of TiO_2 layers on alumina balls

- *Oxidation of metal-coated balls by wet hydrogen*

Figs. 8(a) and 8(b) show the Ti or Sn-coated alumina balls before and after oxidation by wet hydrogen at 980 °C. Before oxidation, the Ti-balls look dull metallic color. However; these exhibit pure white by oxidation (Al_2O_3/TiO_2) as characterized by the rutile phase of TiO_2. A similar result was also obtained for Al_2O_3/SnO_2.


(a) *(b)*

Fig.8 *(a) Ti-coated alumina ball before oxidation (Al_2O_3/Ti)*
(b) Ti-coated alumina ball after oxidation (Al_2O_3/TiO_2)

- *Evaluation of the decomposition ability*

Decomposition experiment of toluene has been carried out, using an external furnace, in a Pyrex tube which includes closely-packed Al_2O_3/TiO_2 balls (Fig. 8). Fig. 9 shows the decomposition of toluene as a function of temperature, where O_2 was bubbled into toluene to prepare saturated vapor of toluene. The gas flow rate was 50 ml/min. Toluene starts decomposing around 250 °C and almost completed at 500 °C. At the same time, the amount of

CO_2 increases remarkably, suggesting that toluene is decomposed to H_2O and CO_2.

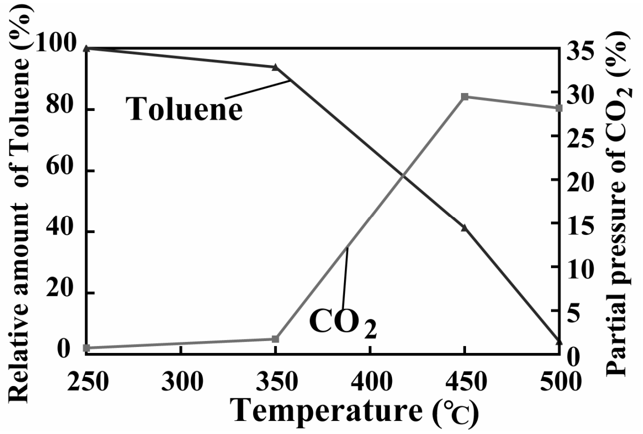

Fig.9 Decomposition of toluene by Al_2O_3/TiO_2 balls.

The same experiment was also performed with Al_2O_3/SnO_2 balls (Fig.10), showing an even better result.

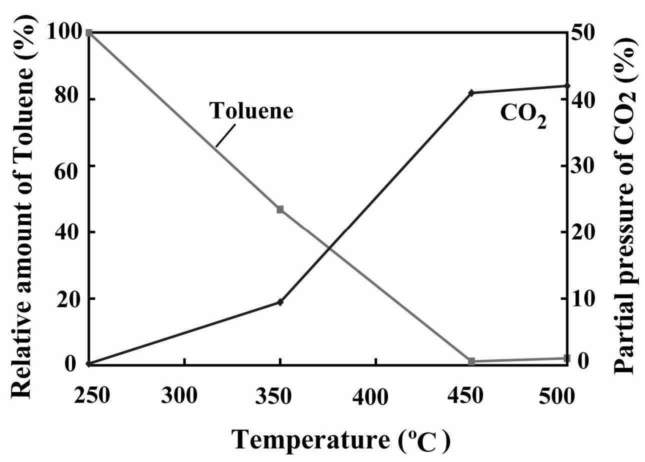

Fig.10 Decomposition of toluene by Al_2O_3/SnO_2 balls.

The above results show that Al_2O_3/TiO_2 or Al_2O_3/SnO_2 balls exhibit a high decomposition ability, but still about one tenth of the ability of ST-01 in powdered form. However, the present all system is quite easy to handle and thus appropriate for decomposition of a relatively small quantity at a slow rate.

5. Conclusions

Fixation of TiO_2 onto substrates has been carriedout by means of two methods: electrophoretic deposition and direct oxidation of metals by wet hydrogen. The conclusions can be summarized as follows.

Fixation of powdered TiO_2 (ST-01) on metal substrates has successfully been achieved by electrophoretic deposition. The TiO_2 layer thus prepared exhibits a high decomposition ability which is almost equivalent to that of powdered TiO_2. The present system is powerful and appropriate for decomposition of a large quantity of VOC at a high rate. The oxide buffer-layer is found to be effective in suppressing the peeling-off of the deposited TiO_2 layer from the core metal.

Ti-coated alumina balls have directly been oxidized by means of wet hydrogen at about 980 °C. The oxide layer is of the rutile form and is fixed firmly on the core alumina ball (TiO_2/Al_2O_3). The TiO_2 layer possess a high decomposition ability, but still about one tenth of the ability of ST-01 in powdered form. However, the present all system is quite easy to handle and thus appropriate for decomposition of a relatively small quantity at a slow rate.

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Author Biography

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