Fixation of powdered TiO_2 onto metal substrates by electrophoretic deposition and its use for complete decomposition of volatile organic compounds

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Abstract

Titanium dioxide was once extensively investigated as a photoconductor for the electrophotographic photoreceptor early on. We are so far involved in complete decomposition of organic wastes as well as volatile organic compounds (VOC) by thermally generated holes in TiO_2*. In view of the practical use of the present system, fixation of* TiO_2 *powders onto a substrate seems to be the core technology. To realize this, we have tried in the present investigation to fix powdered* TiO_2 *onto metal meshes by means of electrophoretic deposition. We have constructed a cartridge which includes ten pieces of mesh disk (25 mm in diameter coated with* TiO_2*) that are arranged vertically. The present system in combination with an external furnace is found to exhibit an excellent performance to completely decompose VOC into* H_2O *and* CO_2 *with a high rate.*

Introduction

TiO_2 was once extensively investigated as a photoconductor for the electrophotographic photoreceptor at the dawn of the electrophotography [1]. Nowadays, it has attracted attention as a material for photocatalyzers [2] and solar cells [3,4]. We have previously shown, for the first time, that polycarbonate (PC) used as a material for optical discs can completely be decomposed in the presence of TiO_2 powders, releasing a huge amount of exothermic energy of about 1.85 kJ/g [5]. Since this moment, we have been conducting a series of investigations on the use of the present technology for complete decomposition of organic wastes (mainly thermoplastic and thermosetting polymers) as well as for removal of diesel exhaust [6-11]. Our system is characterized by the use of thermally excited holes at high temperatures (*e.g.*, about 350 °C) in combination with a molten state of thermoplastics, for example, PC as shown in Fig. 1. A great number of charge carriers are available in TiO_2 at high temperature as shown by the product of the Fermi-Dirac distribution function and the density of states [12]. 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 $n_{623K}/n_{RT} \approx 8.8\times10^{13}$, where $E_g = 3.2$ eV. This number has approximately been confirmed in our previous experiment based on the single crystal of TiO_2 of the rutile phase [7]. This indicates that any semiconductors can basically be used for the present system, provided that they are stable at high temperature in an oxygen atmosphere. Therefore, oxide semiconductors such as SnO_2, ZnO etc. come also 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, ending up with their complete decomposition into H_2O and CO_2 under oxygen or air [7].

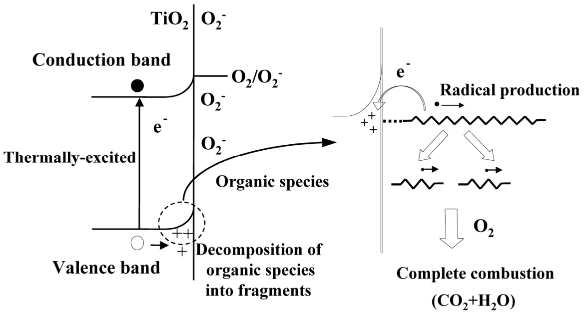

Figure 1. Decomposition process of PC at the "TiO_2/PC" interface by means of thermally generated holes

In our previous studies, we worked with powdered TiO_2 in an autoclave based upon a fluidized bed system. However, the powder system is obviously not adequate for practical applications, especially for decomposition of VOC (volatile organic compound). For this reason, fixation of powdered TiO_2 onto a substrate seems to be one of the core technologies at the moment. Because of this, an attempt has been made in the present investigation to fix powdered TiO_2 onto stainless meshes, or Ni-Cr wires (*i.e.* heat element) by electrophoretic deposition. The electrophoretic deposition method [13] is a technology similar to electroplating and seems to be particularly promising, because this technique enables us to prepare practical devices of any shape with a simple and low cost setup. When we use meshes coated with TiO_2, an external heater is necessary; whereas the Ni-Cr wire coated with TiO_2 requires no external furnace.

This paper deals with the mesh system while the Ni-Cr wire system will be described in the paper which follows this publication.

Experiment

Materials

Commercial TiO_2 powders of ST-01 were obtained from Ishihara Sangyo Kaisha, Ltd. This is of the anatase form with a specific surface of 298 m^2/g (*ca.* 7 nm in average diameter). Tetramethylammonium hydroxide (TMAH: 15 wt% aqueous solution) was obtained from Wako Pure Chemical Industries, Ltd. Acetone of electronic grade and sulfuric acid of guaranteed grade were purchased from Junsei Chemical Co., Ltd. Nitrocellulose of RS-60 $[C_6H_7O_2(NO_2)(OH)]_n$ (n = 360) was obtained from KCNC

Ltd. Ni-Cr wires (0.5 mm in diameter) and SUS304 meshes (wire diameter: 100 μm; spacing: 250 μm) were obtained from NILACO and Kyuho Kinzoku, respectively.

Preparation of a cartridge with mesh disks

A number of mesh disks (diameter: 22 mm) were punched out from the mesh sheet. Then, these were arranged vertically in a stainless cartridge as shown in Fig. 2.

Figure 2. Cartridge system which includes SUS meshes

Preparation of the suspension

The typical composition of the suspension is based upon our previous reports [13]. 10 g of ST-01 was suspended in 100 ml of an acetone solution containing 0.3 g of nitrocellulose. The suspension was conditioned in the presence of zirconia balls by a paint shaker for 30 min. Then, 50 ml of the suspension was placed into an electrolytic cell of 50 ml, and 12 μl of TMAH and 4.0 μl of sulfuric acid were added.

Preparation of a buffer layer

In experiments with Ni-Cr or SUS with TiO_2 layers, we encountered a serious problem that thermal cycles between room temperature and 500 °C caused often tiny cracks to appear in a TiO_2–coated layer, or the layer peeled off due to a large difference in thermal expansion coefficients of Ni-Cr or SUS and TiO_2. However, this draw-back was obviated by introducing a thin buffer layer of Cr_2O_3 between Ni-Cr or SUS and TiO_2. A thin layer of Cr_2O_3 (about 1 μm) was prepared by oxidizing Ni-Cr wires or SUS meshes in wet hydrogen at 980 °C for 1 h, using equipment as shown in Fig. 3.

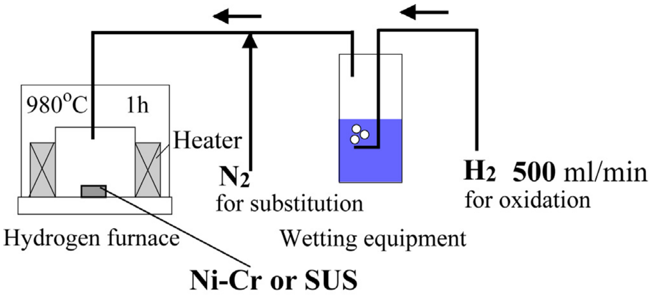

Figure 3. Equipment for oxidation of Ni-Cr wires or SUS meshes by wet hydrogen

Fixation of powdered TiO_2

Fig. 4 illustrates schematically the experimental setup for the electrophoretic deposition. A Ni-Cr wire or SUS mesh with a buffer layer of Cr_2O_3 works as the anode while an Al cylinder was used as the counter electrode. The applied voltage was 100-500 V while the deposition time was varied from 0.01 to 0.1 s.

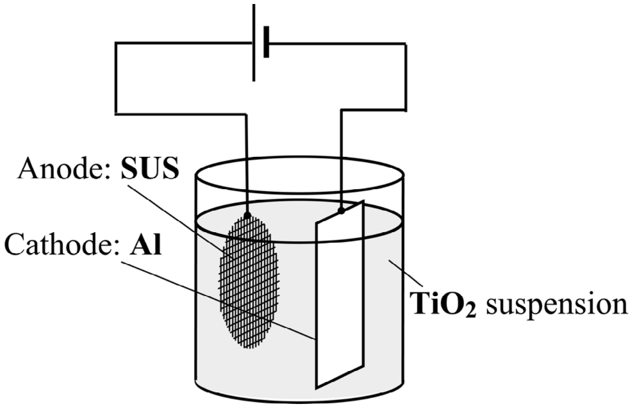

Figure 4. Schematic illustrations of the electrophoretic deposition

Equipment

Scanning electron microscope (SEM) pictures were taken by a VE-8800 from KEYENCE. Raman spectra were measured by an NRS-3100 laser Raman spectrophotometer from JASCO. Specific surface was measured by a Monosorb (LOOP) MS-22 from YUASA IONICS Inc. Quadrupole mass spectrometer (abbreviated to Q-mass: RG-102 from ULVAC) was used for gas analysis.

Experiment for VOC decomposition

Fig. 5 shows the schematic representation of the equipment for VOC decomposition. Toluene was used as a VOC for decomposition experiment. 5 μl per minute of toluene was pumped and vaporized in the vaporizing chamber at 200 °C. 100 ml per minute of air was used as a carrier gas. The toluene concentration was about 1 vol%. This gas was introduced into a reactor chamber and then the decomposed gas was sampled and analyzed by Q-mass.

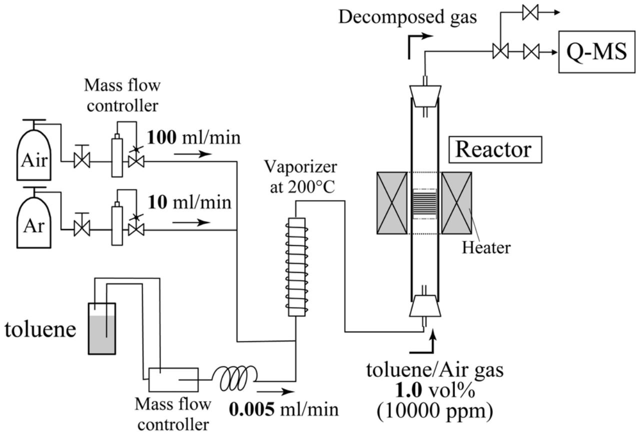

Figure 5. Schematic representation of the equipment for VOC decomposition

Results and Discussion

Identification of the Cr_2O_3 layer

Fig. 6 shows the Raman spectra of the oxide layers prepared on Ni-Cr wires or SUS meshes by wet hydrogen, together with commercially available powdered Cr_2O_3. The spectrum of the oxide on Ni-Cr is in good accord with that of powdered Cr_2O_3 (300, 352, 535, 560, and 625 cm^{-1}), while one additional band appear around 700 cm^{-1} in the spectrum of the oxide on SUS meshes which is presumably due to the $FeCr_2O_4$ [14,15]. These results indicate that the selective oxidation of Cr (*i.e.*, Cr_2O_3) in alloys was successful on both Ni-Cr wires and SUS meshes.

Figs. 7(a) and 7(b) show the SEM pictures with different magnifications of SUS/Cr_2O_3 prepared by wet hydrogen. The surface looks very even and smooth.

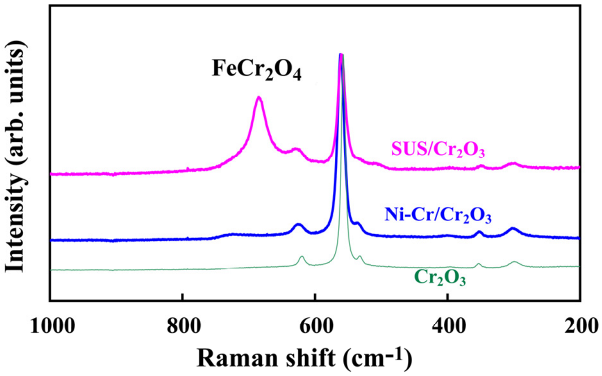

Figure 6. *Raman spectra of SUS/Cr_2O_3, Ni-Cr/Cr_2O_3, and commercially available powdered Cr_2O_3*

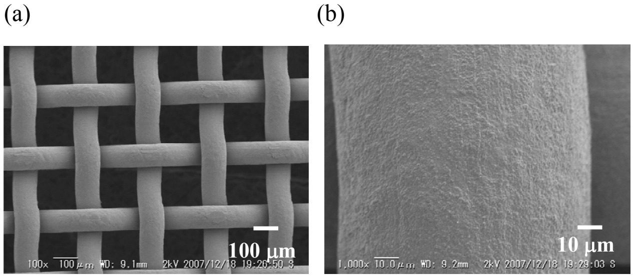
(a) (b)

Figure 7. *SEM pictures with different magnifications of the SUS/Cr_2O_3 prepared by wet hydrogen*

Characteristics of the electrophoretic deposition

Fig. 8 shows the amount of deposit *vs.* deposition time as a function of applied voltages. The amount of deposit increases with time and applied voltage. The amount of deposit shows a saturation tendency as the deposition time is increased. Our target thickness of the deposit layer is about 3-5 µm. So the optimum condition for deposition is: 100 V for 0.01 s.

Figs. 9(a) and 9(b) show the SEM pictures with different magnifications of electrophoretically deposited TiO_2-layer on a SUS/Cr_2O_3 mesh taken at the magnification of 50 and 5000, respectively.

The above sample of SUS/Cr_2O_3/TiO_2 was heat-cycled ten times between room temperature and 500 °C. Neither cracks nor peeling-off of the TiO_2 layer was observed, indicating that the buffer layer is effective in suppressing the cracks and peeling-off.

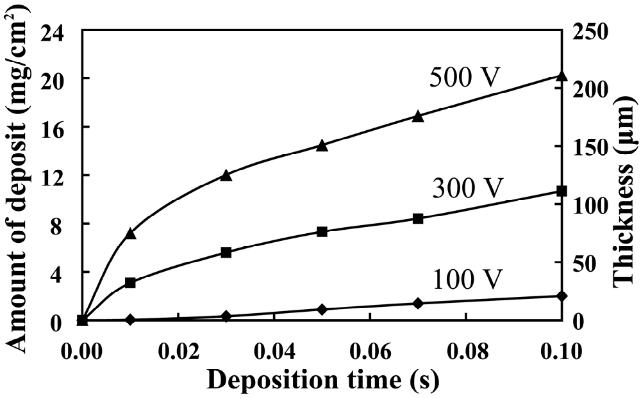

Figure 8. *Amount of deposit vs. time as a function of applied voltage*

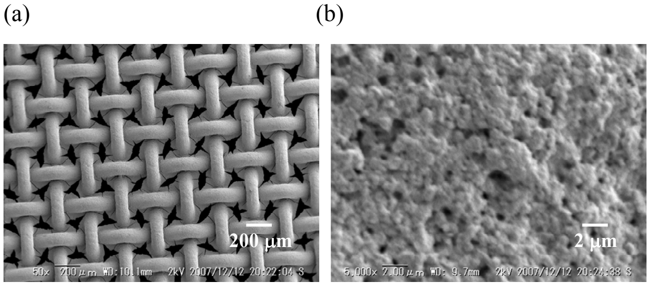
(a) (b)

Figure 9. *SEM pictures with different magnifications of electrophoretically deposited layers on SUS/Cr_2O_3*

Surface area of wire samples

Table 1 shows the surface area of Ni-Cr, Ni-Cr/Cr_2O_3, and Ni-Cr/Cr_2O_3/TiO_2 wires (unit: m^2/cm). The values normalized by that of Ni-Cr are shown on the right column. The surface area of Cr_2O_3 is larger than of Ni-Cr by 13 %. The surface area of TiO_2 is one order of magnitude larger than that of Ni-Cr. This indicates that the large specific surface of original TiO_2 powders is well preserved even in electrophoretically deposited layers.

Table 1 Surface area of Ni-Cr, Ni-Cr/Cr_2O_3, and Ni-Cr/Cr_2O_3/TiO_2

	Surface area (m^2/cm)	Normalized value by that of Ni-Cr
Ni-Cr	2.66×10^{-4}	1.00
Ni-Cr/Cr_2O_3	3.01×10^{-4}	1.13
TiO_2-deposited Ni-Cr/Cr_2O_3	2.60×10^{-3}	9.77

VOC Decomposition experiment with the cartridge system

Decomposition experiment of toluene was carried out, using a cartridge which includes ten pieces of mesh disks with TiO_2, as shown in Fig. 5. Fig. 10 shows the decomposition of toluene as a function of temperature. Toluene starts decomposing around 350 °C and is decomposed about 95 % at 500 °C. At the same time, the amount of CO_2 and H_2O increase remarkably while no other species were detected except for N_2 and O_2 in air. This result indicates that toluene is completely decomposed into H_2O and CO_2.

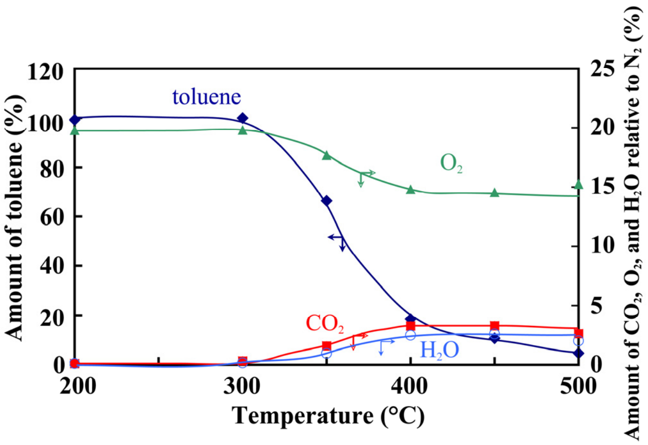

Figure 10. *Decomposition of toluene in air with a cartridge system composed of ten meshes of SUS/Cr_2O_3/TiO_2 as a function of temperature*

Conclusions

A novel system composed of SUS mesh disks (SUS/Cr_2O_3/TiO_2) has been developed for the removal of VOC. The present cartridge system has a honeycomb-like structure and exhibits an excellent performance to completely decompose VOC with a high rate into H_2O and CO_2.

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Author Biography

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