

Fixation of powdered TiO_2 onto Ni-Cr heat elements 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 Ni-Cr wires (i.e. heat element; 0.5 mm in diameter) by means of electrophoretic deposition. The present "heater-built-in" system with TiO_2 is found to possess an excellent decomposition ability of toluene into H_2O and CO_2 . This enables us to realize a compact, practical device with low cost.

1. 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 be completely 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 ($n_{\text{RT}} = n_0 \exp[-E_g/2kT_{\text{RT}}]$ and $n_{623\text{ K}} = n_0 \exp[-E_g/2kT_{623\text{ K}}]$, 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 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 cation radicals by thermally generated holes, followed by their propagation throughout the

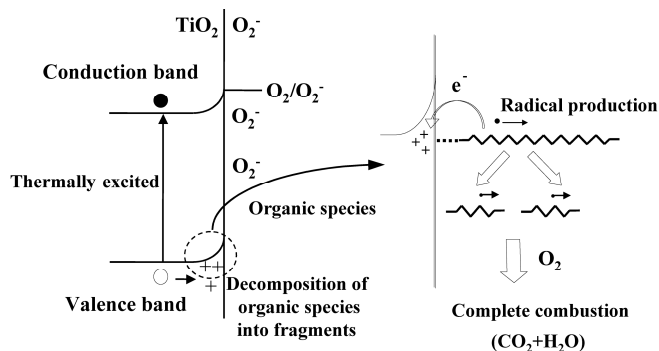


Figure 1. Decomposition process of PC at the " TiO_2/PC " interface by means of thermally generated holes.

polymer chain to break PC into small fragments, ending up with their complete decomposition into H_2O and CO_2 under oxygen or air [7].

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 steel 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 Ni-Cr wire system while the mesh system will be described in the paper which appears before this publication in the NIP proceedings (2008).

2. Experiment

2-1. 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) were obtained from NILACO.

2-2. 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 μ l of TMAH and 4.0 μ l of sulfuric acid were added.

2-3. Preparation of a buffer layer

In experiments with Ni-Cr 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 and TiO_2 . However, this drawback was obviated by introducing a thin buffer layer of Cr_2O_3 between Ni-Cr and TiO_2 . A thin layer of Cr_2O_3 (about 1 μ m) was prepared by oxidizing Ni-Cr wires in wet hydrogen at 980 °C for 1 h, using equipment as shown in Fig. 2.

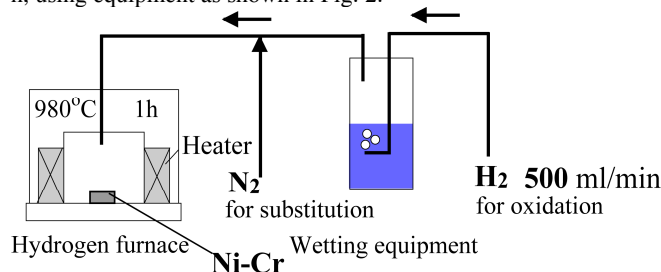


Figure 2. Equipment for oxidation of Ni-Cr wires by wet hydrogen.

2-4. Fixation of powdered TiO_2

Figs. 3(a) and 3(b) illustrate schematically the experimental setup for the electrophoretic deposition. A Ni-Cr wire or coil 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.

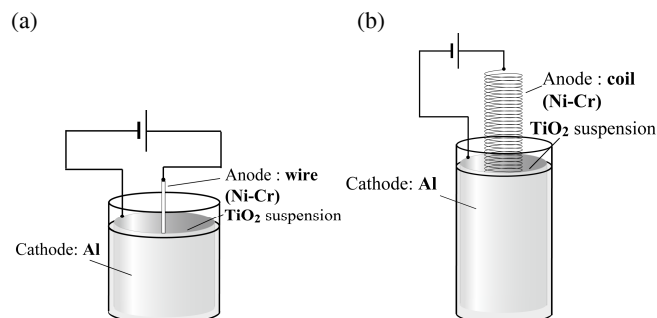


Figure 3. Schematic illustration of the electrophoretic deposition: (a) Ni-Cr wire and (b) Ni-Cr coil.

2-5. 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 (abbreviate to Q-mass: RG-102 from ULVAC) was used for gas analysis.

2-6. Experiment for VOC decomposition

Fig. 4 shows the three-coaxial device for VOC decomposition (size: 26 mm in diameter and 200 mm long cylinder). We constructed a three-coaxial glass tube, each of which was wound with Ni-Cr/ Cr_2O_3 / TiO_2 wires. This device was placed in a reactor of the equipment for VOC decomposition as shown in Fig. 5.

In the present experiment, toluene was used as a VOC for decomposition experiment. 2.5 μ l per minute of toluene solution was pumped and vaporized in the vaporizing chamber at 200 °C. 50 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 4. Three-coaxial wire system.

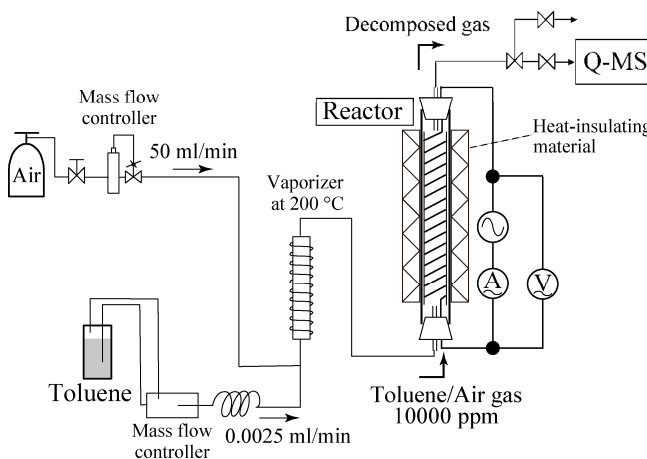


Figure 5. Schematic representation of the equipment for VOC decomposition.

3. Results and Discussion

3-1. Identification of the Cr_2O_3 layer

Fig. 6 shows the Raman spectra of the oxide layers prepared on Ni-Cr wires 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}), showing that the selective oxidation of Cr in an alloy to Cr_2O_3 was successful on Ni-Cr wires by wet hydrogen.

Figs. 7(a) and 7(b) show the SEM pictures with different magnifications of Ni-Cr/ Cr_2O_3 prepared by wet hydrogen. The

surface looks very smooth at the magnification of 100, while some bumpy structures can be seen at the magnification of 5000 [14].

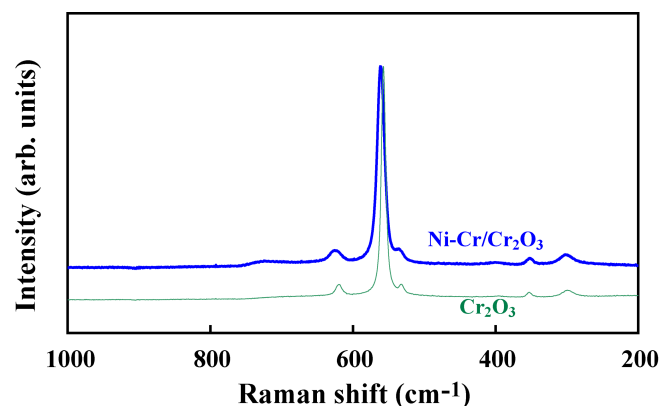


Figure 6. Raman spectra of the oxidized Ni-Cr and commercially available powdered Cr_2O_3 .

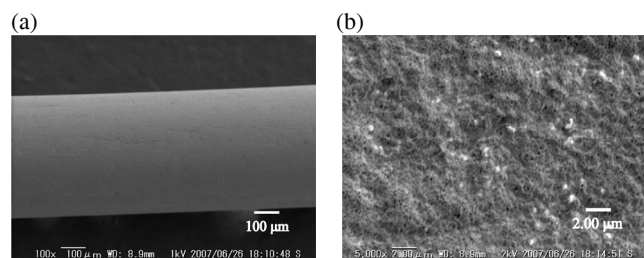


Figure 7. SEM pictures with different magnifications of the Ni-Cr/ Cr_2O_3 prepared by wet hydrogen.

3-2. 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.

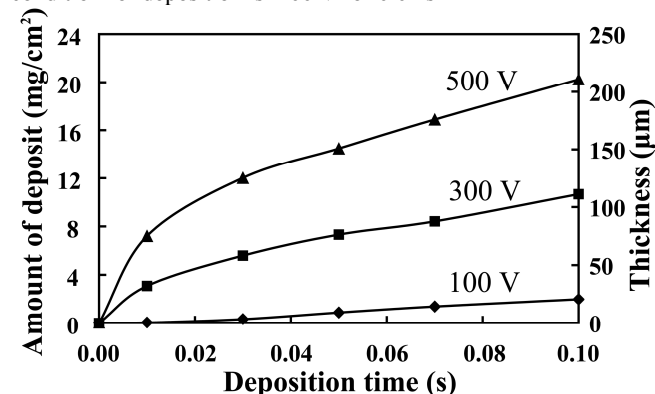


Figure 8. Amount of deposit vs. time as a function of applied voltage.

Figs. 9(a) and 9(b) show the SEM pictures with different magnifications of electrophoretically deposited TiO_2 -layer on a Ni-Cr/ Cr_2O_3 wire taken at the magnification of 100 and 1000, respectively. The surface of the TiO_2 layer looks homogeneous and even.

The above sample of Ni-Cr/ Cr_2O_3 / TiO_2 was heat-cycled ten times between room temperature and 500 $^{\circ}\text{C}$. Neither crack nor peel-off of the TiO_2 layer was observed, indicating that the buffer layer is effective in suppressing the cracks and peel-off.

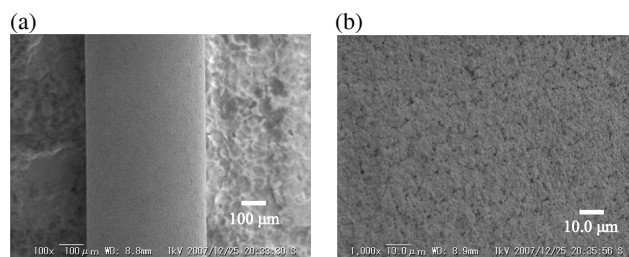


Figure 9. SEM pictures with different magnifications of electrophoretically deposited layers on Ni-Cr/ Cr_2O_3 .

3-3. Surface area of wire samples

Table 1 shows the surface area per cm (m^2/cm) of Ni-Cr, Ni-Cr/ Cr_2O_3 , and Ni-Cr/ Cr_2O_3 / TiO_2 wires. The values normalized by that of Ni-Cr are shown on the right column. The surface area of Cr_2O_3 is larger than that 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

3-4. VOC decomposition experiment with the “heater-built-in” system (Ni-Cr/ Cr_2O_3 / TiO_2)

Fig. 10 shows the decomposition of toluene as a function of power consumption or as a function of temperature. Toluene decomposition starts around 230 $^{\circ}\text{C}$ and is nearly completed at about 550 $^{\circ}\text{C}$. The power consumption at this point amounts to about 87 W. The decomposition of toluene is accompanied by the decrease of O_2 and increase of CO_2 and H_2O . No additional fragments of toluene could be observed in the mass spectra monitored by Q-mass during the decomposition process. The present experiment suggests that our novel “heater-built-in” system (Ni-Cr/ Cr_2O_3 / TiO_2) basically works well and can be a compact, high-performance system with low costs in the future.

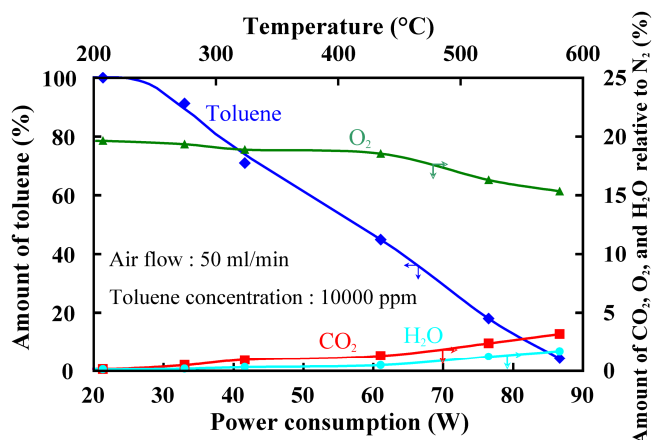


Figure 10. Decomposition of toluene in air with a "heater-built-in" system (Ni-Cr/Cr₂O₃/TiO₂) as a function of power consumption or temperature.

4. Conclusions

A novel "heater-built-in" system (Ni-Cr/Cr₂O₃/TiO₂) has been developed for the removal of VOC. Our targeted function for the VOC decomposition has been confirmed in the present investigation. Further research and development are directed toward improvement of the system efficiency.

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