VOC Decomposition System Based upon Heater-Integrated Catalyst Units Using NiO or Cr₂O₃

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We have previously shown that oxide semiconductors (TiO₂, NiO, Cr₂O₃, etc.) exhibit remarkable catalytic effects when heated at high temperatures of about 350–500°C and that the effect has been interpreted in terms of the formation of a large number of highly oxidative holes caused by thermal excitation of semiconductors. This prompted us to utilize this technology for complete removal of volatile organic compounds (VOCs). In the present investigation, we aim at constructing a compact device for practical implementation composed of four-stacked “heater/honeycomb” units. Each unit comprises a spiral Ni-Cr heater as well as a honeycomb plate coated with powdered NiO or Cr₂O₃. Decomposition experiment was carried out in the range from room temperature to 500°C, using 10000 ppm toluene as the VOC at a flow rate of 10 l/min. As a result, the toluene decomposition was found to begin at about 100°C and was completed (i.e., 0 ppm) at about 300°C, showing an excellent decomposition characteristic in both NiO and Cr₂O₃. [doi:10.2320/matertrans.M2010105]

(Received March 19, 2010; Accepted April 27, 2010; Published June 16, 2010)

Keywords: volatile organic compound, oxide semiconductor, thermal activation, NiO, Cr₂O₃

1. Introduction

Volatile organic compounds (VOCs) are emitted into the atmosphere due to various human activities, for example, unburned fuel from power production, transportation, and solvents from painting or printing industries.¹⁾ Particle emission from office printers (i.e., emission of monomers from fusers) causes also an environmental problem.²⁾ Furthermore, in houses and buildings, VOC such as formaldehyde emitted from floor and furniture materials is harmful to human health.³⁾ Consequently, VOC causes serious environmental issues, such as photochemical smog, sick house syndrome etc.¹⁾ In view of the present situation, we started our investigation on complete removal of VOC and organic wastes by means of thermally excited holes in oxide semiconductors such as TiO₂,^{4–13)} NiO,¹⁴⁾ Cr₂O₃,^{15,16)} and α -Fe₂O₃.¹⁷⁾ at about 350–500°C. The use of thermally generated holes for removal of VOC and organic wastes is an entirely new technology initiated by us in 2001.⁴⁾ The present technology dates back to our accidental finding that the catalytic effect suddenly appears when oxide semiconductors are heated at high temperatures of about 350–500°C. This is due to the formation of a large number of highly oxidative holes caused by thermal excitation of semiconductors. Lasers, transistors, and diodes are the representative applications of semiconductors. However, ours is the application that utilizes semiconductive properties at high temperatures.

The availability of a large number of holes at high temperatures in semiconductors will be explained in the following way. The number of charge carriers in semiconductors, for example, in TiO₂, is shown by the product of the Fermi-Dirac distribution function and the density of states.¹⁸⁾ The number of carriers estimated by above calculation at room temperature (RT) and 350°C ($n_{RT} = n_0 \exp[-E_g/2k_B T_{RT}]$ and $n_{623K} = n_0 \exp[-E_g/2k_B T_{623K}]$, respectively) gives a ratio of $n_{623K}/n_{RT} \approx 8.8 \times 10^{13}$ where $E_g = 3.2$ eV is the band gap of TiO₂ of the rutile phase. This

Fig. 1 Decomposition mechanism of PC by the use of thermally generated holes in TiO₂.

number has approximately been confirmed in our experiment using single crystals of TiO₂ of the rutile phase.⁷⁾

Figure 1 shows an example of the complete decomposition of polycarbonate (PC) used as the substrate for optical discs.^{6,7)} The initial process of decomposition is the capture of bonded electrons from PC to form cation radicals there by thermally generated holes, followed by their propagation through the substance to break giant molecules into fragments.⁸⁾ This results in the complete decomposition of PC into H₂O and CO₂. The thermal activation described above has two important functions: one is to create a vast number of holes at high temperatures, and the other is to fragment large molecules into small pieces through radical splitting at high temperatures, so that the fragment can easily react with oxygen to yield H₂O and CO₂.

As the first step in our trial for practical implementation, we fixed semiconductor powders (TiO₂, NiO, and Cr₂O₃) onto a cylindrical honeycomb substrate and heated externally using a tube-shaped furnace.^{11–15)} This system operated perfectly well with honeycombs of a small cross-sectional area. However, it soon became clear that the core part of the honeycomb unit cannot sufficiently be heated with increasing diameter of cylindrical honeycombs. This results in an accumulation of incomplete decomposition products of dark color. In order to circumvent this problem, we cut the cylindrical honeycomb in round slices and sandwiched each

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Fig. 2 Schematic illustration of the honeycomb system composed of four-stacked "heater/honeycomb" units.

Fig. 3 (a) Schematic illustration of the thermal insulator with a Ni-Cr wire as the heat element and (b) Cr_2O_3 -coated honeycomb substrate.

slice with heat elements, so that each catalyst-coated slice can effectively and uniformly be heated. This is our novel system that is reported in the present paper.

2. Basic Design of Heater-Integrated Catalyst Units for VOC Decomposition

As schematically shown in Fig. 2, our catalyst system is composed of four-stacked catalyst-units. Each unit includes one Ni-Cr heater embedded in a thermal-insulator substrate [Fig. 3(a)] and one catalyst-coated honeycomb plate [Fig. 3(b): $10\text{ cm} \times 10\text{ cm} \times 1\text{ cm}^{\text{H}}$]. The dimension of the heater-embedded insulator [Fig. 3(a)] is $16\text{ cm} \times 16\text{ cm} \times 2\text{ cm}^{\text{H}}$. There are two windows in the middle of the thermal insulator for the VOC flow (each size: $9\text{ cm} \times 4.5\text{ cm}$). On the front of the insulator, there is a groove for a spiral Ni-Cr wire; whereas, on the rear, there is a cavity for the honeycomb

Fig. 4 Catalyst unit which includes a Ni-Cr wire on the front and a Cr_2O_3 -coated honeycomb plate on the rear.

Fig. 5 Schematic representation of the equipment for VOC decomposition with the catalyst system.

plate [Fig. 3(b)] to be installed. Figure 4 shows the heater-integrated catalyst unit in practice which includes a Ni-Cr heater and a Cr_2O_3 -coated honeycomb plate. Then, the four catalyst-units are stacked in pile as shown in Fig. 5 as represented by the catalyst system.

3. Experimental

3.1 Materials

NiO powders (purity: 99%; specific surface: $1\text{ m}^2/\text{g}$) and Cr_2O_3 powders (purity: 99%; specific surface: $3\text{ m}^2/\text{g}$) were obtained from Junsei Chemical Co., Ltd. Spiral Ni-Cr wires (4 mm in diameter and 60 cm long: 400 W) were purchased from Sakaguchi E.H Corp. Cordierite honeycomb substrates ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) with 200 cells per square inch (cps) were purchased from Kyocera Corporation (dimension: $10\text{ cm} \times 10\text{ cm} \times 1\text{ cm}^{\text{H}}$). Nitrocellulose of RS-60 [$\text{C}_6\text{H}_7\text{O}_2(\text{NO}_2)(\text{OH})_n$ ($n = 360$)¹⁹] was purchased from Korea CNC Ltd. Acetone and toluene of guaranteed grade were obtained from Junsei Chemical Co., Ltd.

3.2 Annealing of Ni-Cr wires in wet hydrogen

The Ni-Cr wire was annealed in advance in wet hydrogen at 980°C for 1 h^{13,15)} in order to make the wire soften, so that the wires could easily be fixed in the groove of the thermal

insulator [Fig. 3(a)]. The present annealing was also effective in selectively oxidizing Cr in Ni-Cr wires to greenish Cr₂O₃ on the surface (i.e. about 1 μ m). The Cr₂O₃-layer was expected to partly serve as an oxide semiconductor for VOC decomposition. However, its effect was found to be quite small due to its small surface area as compared with the NiO- or Cr₂O₃-coated honeycomb plate with a large area.

3.3 Fixation of catalyst powders onto honeycomb substrates

Dip method was employed to deposit powdered oxide-semiconductors onto honeycomb substrates. The suspension used was composed of a ketonic solvent, a minute amount of nitrocellulose as the dispersant or surface active agent, and powdered substances of metal oxides.^{20,21)} The fixation was carried out as follows. 30 g of NiO or Cr₂O₃ powders was first dried in air at 200°C for 1 h to eliminate water moisture. The powder was then suspended in 600 ml of an acetone solution containing 3.0 g of nitrocellulose. The suspension was conditioned in the presence of zirconia balls (0.6 mm in diameter) by a single-arm paint-shaker for 30 min (model 5410 from Red Devil Equipment Co.).

A honeycomb substrate to be coated was first dried at 200°C in air for 24 h. Then, the substrate was dipped into the suspension for 10 s. After that, the coated substrate was dried in an oven at 200°C for 30 min. During this process, the nitrocellulose used was thermally decomposed around 180°C.

3.4 Catalyst system composed of the stacked “heater/honeycomb” units

Four pieces of the catalyst unit were stacked in pile and bolted together to constitute a stand-alone catalyst-system as shown in Fig. 5, where there were two additional thermal insulators A and B on both sides of the piled units. VOC was then made to flow through a series of the catalyst units horizontally. The temperature was controlled with a thermocouple placed at the entrance honeycomb-plate near the inlet. The present system is quite flexible, because we can stack the catalyst units as many as possible and also employ a variety of honeycomb substrates with different cell numbers, depending on the VOC flow rate.

3.5 Equipment for VOC decomposition

Figure 5 shows the schematic representation of the equipment for VOC decomposition, using the catalyst system as a reactor. Toluene was used as the representative VOC for decomposition experiment. The toluene concentration at the inlet was about 1 vol% (10000 ppm) and the air was used as the carrier gas at a flow rate of 10 l/min. The outlet gas was analyzed as a function of temperature by means of a GC-2014 gas chromatograph (Shimadzu Corporation).

4. Decomposition Characteristics Using Toluene as the VOC

Figure 6 shows the decomposition characteristic of toluene with the catalyst system based on NiO or Cr₂O₃-coated honeycomb substrates. In both experiments, toluene decomposition begins at about 100°C and is completed at 300°C. However, the amount of undecomposed toluene is lower with

Fig. 6 Decomposition characteristic of toluene as a function of temperature.

NiO in the whole temperature range than that with Cr₂O₃. As far as the onset and complete decomposition temperatures are concerned, no significant difference is recognized between the NiO and Cr₂O₃ systems.

5. Conclusions

A novel catalyst system based upon heater-integrated catalyst units using NiO or Cr₂O₃ has been developed for VOC removal. Complete decomposition of toluene was achieved around 300°C, indicating that the present system exhibits excellent performance for the abatement of VOC.

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