

High sensitive hydrocarbon gas sensor utilizing cataluminescence of $\gamma\text{-Al}_2\text{O}_3$ activated with Dy^{3+}

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Abstract

A new method using cataluminescence (CTL)-based gas-sensor detecting hydrocarbon in air is proposed. CTL is a kind of chemiluminescence (CL), which is emitted during catalytic oxidation of organic vapors, e.g., ethanol and acetone. By depositing Dy on the $\gamma\text{-Al}_2\text{O}_3$ catalyst, we measured the extra CTL spectrum due to Dy^{3+} during the catalytic oxidation of hydrocarbon gas, while no such CTL was emitted from the $\gamma\text{-Al}_2\text{O}_3$ catalyst without Dy. By investigating the luminescence mechanism of Dy, the existence of active species produced in a course of catalytic oxidation to excite Dy directly was clarified. The CTL-based gas-sensor using $\gamma\text{-Al}_2\text{O}_3$ activated with Dy^{3+} has high sensitivity and linear characteristic. The detection limit of *iso*-butane in air is 0.2 ppm. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Recently, a worldwide scale environmental contamination is becoming one very serious problem. As hydrocarbon gases are one of the contaminating substances to produce oxidants in air, the measurement of these gases is necessary for following up the cause of the contamination. A high-sensitive, stable and precious portable gas-sensor is expected for quantitative measurement of these gases of very low concentrations. Development of a new gas-sensor, which has high sensitivity like a semiconductor gas-sensor and stability like a catalytic combustion gas-sensor, is desired.

We have investigated cataluminescence (CTL)-based gas-sensor for measuring concentrations of organic vapors in air using aluminum oxide ($\gamma\text{-Al}_2\text{O}_3$) catalyst [2–8]. CTL is a kind of chemiluminescence (CL) emitted during catalytic oxidation, and was found by Breysse et al. in 1976 [1]. This kind of sensors has many advantages; (1) the quick response, faster than 1 min, (2) the long-term stability and good reproducibility, and (3) the large S/N

(signal to noise) ratio, which enables us to measure the gas concentration lower than 1 ppm. The sensor system is composed of a solid-state catalyst, which converts the gas concentration into the luminescence intensity, and a light detector. Because of the recent development of the small and highly sensitive light detector, the gas sensing based on CL is becoming one effective method.

Breysse et al. [1] have reported that CTL is observed during catalytic oxidation of carbon monoxide on ThO_2 . We observed CTL by vapors of alcohol, ketone and carboxylic acid on $\gamma\text{-Al}_2\text{O}_3$. CTL by hydrocarbon gases, however, has not been reported so far. In the present paper, we describe a new CTL-based sensor realized on the basis of our findings that CTL is emitted from $\gamma\text{-Al}_2\text{O}_3$ catalyst activated with rare-earth in air containing hydrocarbon gases.

2. Experimental

Fig. 1a and b show schematic diagrams of the experimental apparatus for investigating the CTL-based gas-sensor. The area enclosed with a broken line denotes the main components of the CTL-based sensor system. Two

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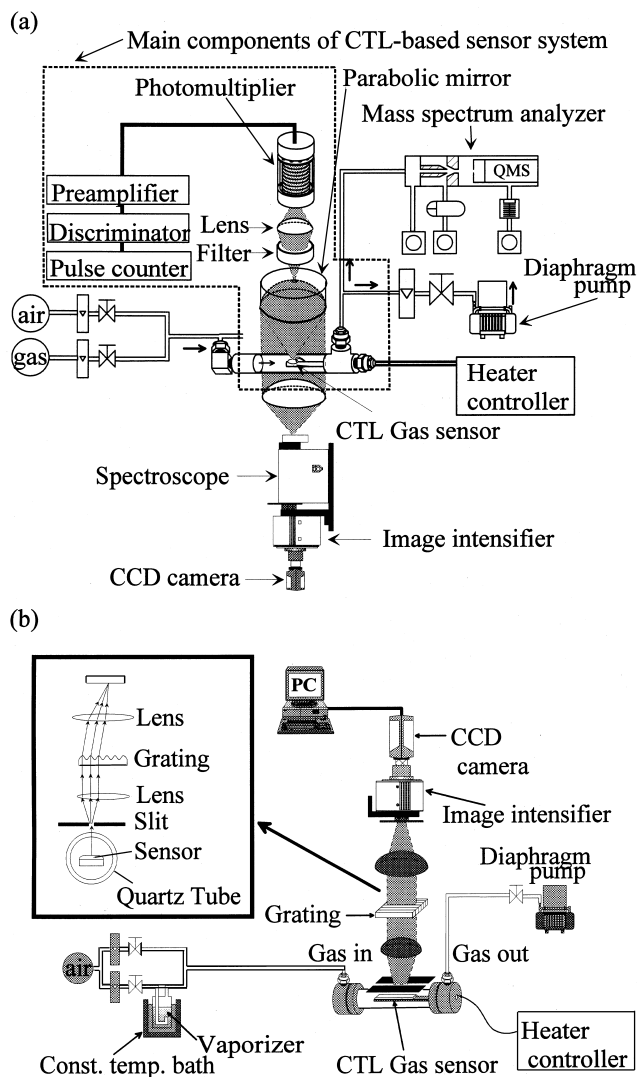


Fig. 1. Schematic diagram of CTL-based gas-sensor and experimental apparatus. (a) A system measuring CTL intensity, CTL spectrum and catalytic reaction products, simultaneously. (b) A system measuring spatial distribution of CTL spectra on three layers along the gas flow.

kinds of catalyst powders were prepared. One is $\gamma\text{-Al}_2\text{O}_3$ powder (for column chromatography) and the other is the $\gamma\text{-Al}_2\text{O}_3$ powder mixed and ground for 3 h with Dy_2O_3 powder of 1 mol%. A CTL-based sensor was made by sintering a layer of the catalyst powder mixed with aqueous solution of $\text{Al}(\text{NO}_3)_3$ as binder on a cylindrical ceramic heater of 3.4 mm in diameter. The CTL intensity at a certain wavelength was measured by a photomultiplier tube (Hamamatsu R464) through optical filters (Fig. 1a). The CTL was dispersed by a spectroscopy and intensified by a photon-imaging head (Hamamatsu C2166), and the CTL spectrum image was measured by photon counting technique using a CCD camera with an image processor (Fig. 1b). The ion intensities of the catalytic reaction products were measured simultaneously by a mass spec-

trimeter. The details of the apparatus were reported elsewhere [7].

3. Results and discussion

3.1. Working mechanism of the sensor

In the CTL measurements during catalytic oxidation of ethanol vapor on $\gamma\text{-Al}_2\text{O}_3$, the CTL component peaking at 420 nm (Fig. 2a) is caused by the excited formaldehyde produced in a course of catalytic oxidation [7]. On the other hand, the extra CTL component of line spectrum is observed for the $\gamma\text{-Al}_2\text{O}_3$ catalyst activated with Dy_2O_3 (Fig. 2b). Similar effect was observed for the specimen activated with another rare earth of Eu or Lu, and the extra CTL spectra were consistent with the emission spectra due to electronic transitions within each rare-earth. Furthermore, the same extra CTL spectrum component was observed by the oxidation of methanol and hydrocarbon gases (e.g., ethylene and butane) on the $\gamma\text{-Al}_2\text{O}_3\text{:Dy}$ catalyst, which do not produce the 420-nm band due to the excited formaldehyde (Fig. 3a, b and c).

We investigated the excitation mechanism of Dy by the following experiments. Fig. 4b shows the illustration of the specimen to examine the effect of the $\gamma\text{-Al}_2\text{O}_3$ catalyst on the extra CTL emission. The specimen consists of three parts of (2) Dy_2O_3 - , (3) $\gamma\text{-Al}_2\text{O}_3$ - and (4) Dy_2O_3 -

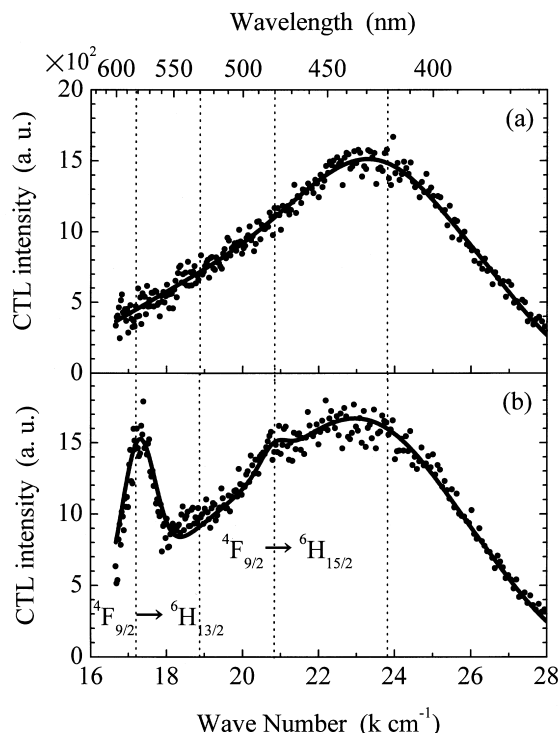


Fig. 2. CTL spectra in air containing ethanol vapor of 500 ppm on (a) $\gamma\text{-Al}_2\text{O}_3$ and (b) $\gamma\text{-Al}_2\text{O}_3\text{:Dy}$ at 450°C.

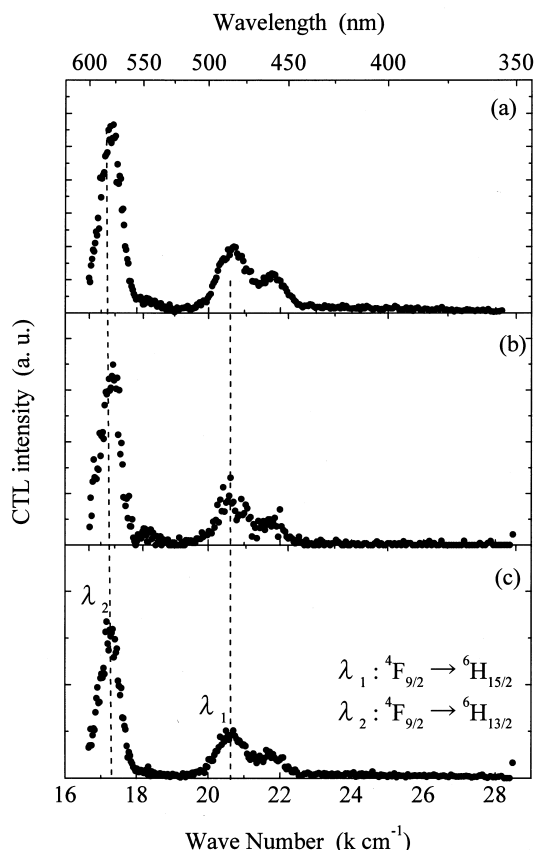


Fig. 3. CTL spectra of (a) methanol of 1000 ppm, (b) ethylene of 2000 ppm and (c) *iso*-butane of 5000 ppm in air on γ - Al_2O_3 :Dy at 450°C.

sintered layers on (1) a ceramic heater with narrow spaces (2-mm width), which prevent the diffusion of electrons and holes between three parts. The specimen was placed in a quartz tube through which a gas of a certain concentration flows at a constant flow-rate to the direction shown by arrows. A thin slit and a grating were placed instead of spectroscopie in Fig. 1a for the measurement of spatial distribution of CTL spectra at these three parts on the specimen along the gas flow (Fig. 1b). The details of this system were reported elsewhere [8].

Fig. 4a shows the spatial distribution of the CTL intensity at 380–620 nm on the specimen kept at 400°C in a flow of air containing ethanol of 2500 ppm. Curve 1 shows the CTL intensity from the specimen without γ - Al_2O_3 layer (3) in Fig. 4b, and curve 2 shows that from the specimen with γ - Al_2O_3 layer (3). Fig. 4c, d and e show CTL spectra at each portion (2), (3) and (4), respectively. For the specimen without γ - Al_2O_3 layer, the CTL is scarcely observed (curve 1). For the specimen with γ - Al_2O_3 layer, the luminescence at the portion (4) is increased three times more than that without γ - Al_2O_3 layer, and the CTL spectrum (Fig. 4e) agrees with the characteristic spectrum due to Dy^{3+} (580 nm for $^4F_{9/2}$ to $^6H_{13/2}$ and 480 nm for $^4F_{9/2}$ to $^6H_{15/2}$ transitions) [9]. On the other hand, the CTL spectrum (Fig. 4d) observed at the

portion (3) results from formaldehyde produced by catalytic oxidation of ethanol, and the CTL intensity shown in curve 2 in Fig. 4a is owing to CTL from the portion (3) (Fig. 4d) and the portion (4) (Fig. 4e). These directly show that certain chemical species were produced in a course of catalytic oxidation on γ - Al_2O_3 and were transferred to the portion (4) to excite Dy^{3+} . Some of the species may be transferred to the portion (2) under turbulent flow and the small increment in the CTL intensity at the portion (2) may contribute to curve 2 in Fig. 4a.

For the CTL-based sensor made of γ - Al_2O_3 catalyst activated with Dy_2O_3 , it is plausible that Dy^{3+} on the catalyst surface is excited by active intermediates produced on γ - Al_2O_3 catalyst during catalytic oxidation.

Similar experiments were conducted for *iso*-butane of 1000 ppm at a catalyst temperature of 500°C. In this case, significant increase in luminescence intensity at the portion (4) was not observed by the addition of the (3) γ - Al_2O_3 catalyst. The intense luminescence of Dy^{3+} , however, was observed when fine Dy_2O_3 powder is dispersed on the γ - Al_2O_3 -sintered layer. The luminescence of Dy^{3+} did not increase after heat treatment of the catalyst at 900°C for 1 h. This implies that Dy^{3+} is excited by adsorbates produced by catalytic oxidation of *iso*-butane. Thus, the luminescence of Dy^{3+} may be observed by hydrocarbon gases, which produce active intermediates but do not produce excited luminous species.

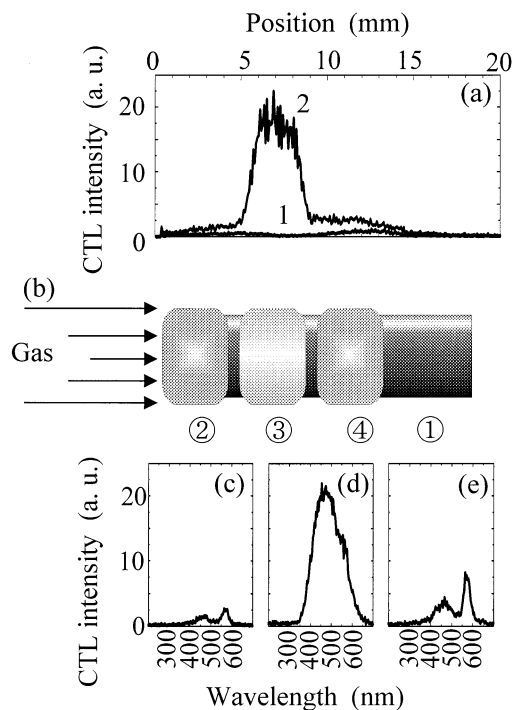


Fig. 4. CTL intensity and spectra at (2) Dy_2O_3 -, (3) γ - Al_2O_3 - and (4) Dy_2O_3 -sintered layers on (1) a ceramic heater (400°C) along the flow of air containing 2500 ppm ethanol. (a) Spatial distribution of the CTL intensity at 380–620 nm, and (b) schematic illustration of the specimen. (c), (d) and (e) are the CTL spectra at each portion (2), (3) and (4), respectively.

3.2. Characteristics of the CTL-based hydrocarbon sensor

The characteristics of the $\gamma\text{-Al}_2\text{O}_3\text{:Dy}$ CTL-based sensor were measured to determine an appropriate working condition as follows. Fig. 5 shows temperature dependence of the CTL intensity I at 580 nm and the ion intensity P of $m/e = 44$ (carbon dioxide) obtained by mass spectrum measurement of a gas at the downstream of the sensor. The air containing *iso*-butane of 100 ppm has a constant flow rate of 10 ml/min. The $\log I$ vs. $1/T$ plots and $\log P$ vs. $1/T$ plots show almost the same activation energy (1.1 eV) in the lower-temperature region. As the amount of the final products of the catalytic oxidation, i.e., carbon dioxide, corresponds to an index of the total reaction rate, the rate of luminous reaction may be controlled by a certain process within catalytic oxidation. Therefore, the CTL intensity may be stable under the diffusion-controlled condition of catalytic oxidation. Although complete diffusion-controlled condition, where the total reaction rate scarcely depends on the catalyst temperature, cannot be established in the temperature range of curve 2 in Fig. 5, the slope of the curve is inclined to saturate at high temperatures. Thus, good reproducibility and quick response are realized at high temperatures under nearly diffusion-controlled condition as shown in Fig. 6a. At the low temperature under reaction-controlled condition, however, poor reproducibility and slow response are observed (Fig. 6b).

The concentration dependence of the CTL intensity for *iso*-butane and propane are shown by curves 1 and 2, respectively, in Fig. 7. The sensor can detect gas in a wide concentration range from 0.2 to 1000 ppm under this

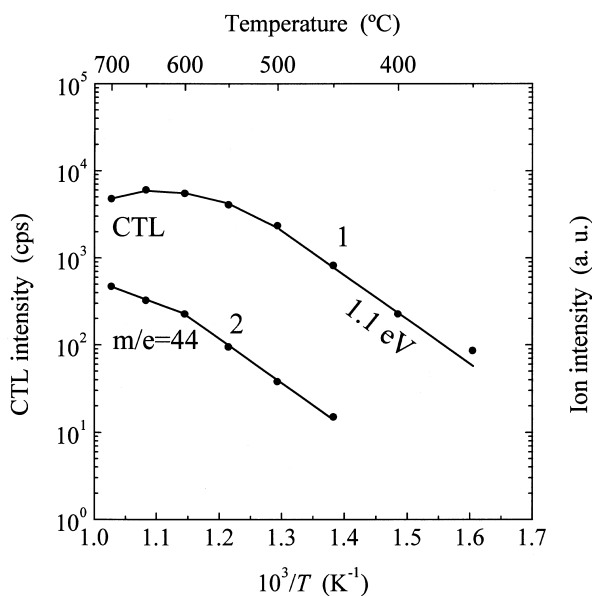


Fig. 5. Temperature dependence of CTL intensity at 560–600 nm (curve 1), ion intensity of the reaction product ($m/e = 44\text{:CO}_2$) by catalytic oxidation (curve 2) on $\gamma\text{-Al}_2\text{O}_3\text{:Dy}$ -sintered layer in air containing *iso*-butane of 100 ppm (flow rate = 10 ml/min).

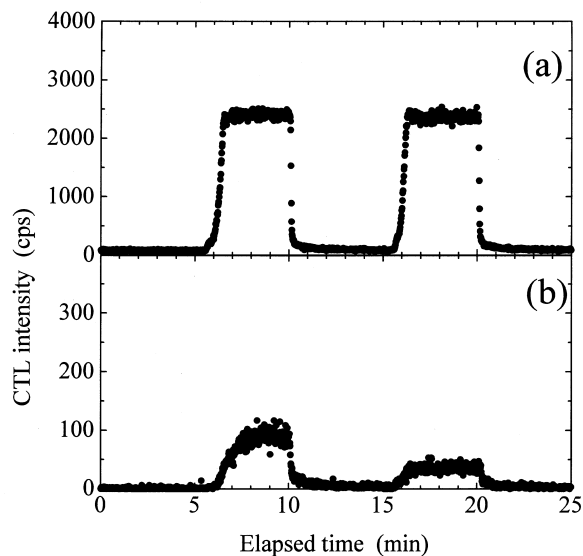


Fig. 6. Response of CTL intensity at 560–600 nm to the injection of *iso*-butane of 100 ppm into an ambient air atmosphere of $\gamma\text{-Al}_2\text{O}_3\text{:Dy}$ -sintered layer at (a) 500°C and (b) 350°C.

measuring condition. High S/N ratio (2 at 0.2 ppm) was obtained by measuring CTL at wavelengths < 500 nm to reject the incandescent radiation from the sensor. The sensor has linear characteristics in the region below 10 ppm, but has sub-linear characteristics at higher concentrations. The diffusion-controlled condition may hardly be established at the higher concentrations at this catalyst temperature of 500°C. The linearity will be improved at higher temperatures.

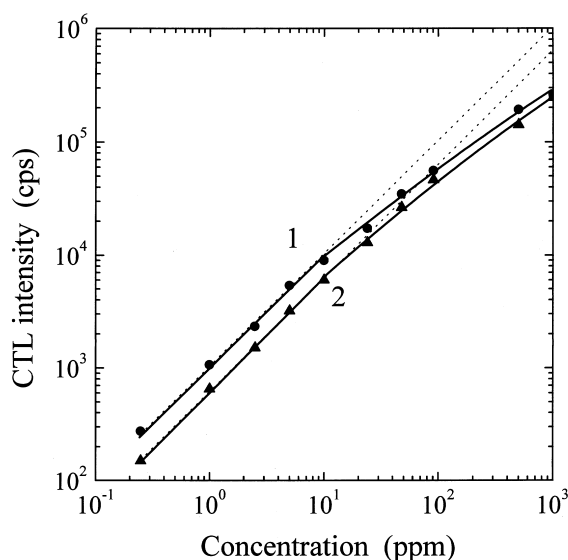


Fig. 7. The concentration dependence of CTL intensity for *iso*-butane (curve 1) and propane (curve 2). The CTL between 400 and 500 nm was measured on $\gamma\text{-Al}_2\text{O}_3\text{:Dy}$ -sintered layer at 500°C.

4. Conclusion

CL during the catalytic oxidation of organic vapors and hydrocarbon gases is observed for the γ -Al₂O₃ catalyst activated with rare earth, e.g., Dy, Eu or Lu. The emission spectra agree with spectra due to the electronic transitions in these ions. By using such activated catalyst, CTL is observed also for gases, which do not produce luminous species in a course of catalytic oxidation on γ -Al₂O₃. This phenomena can be utilized to the CTL-based sensor made of γ -Al₂O₃:Dy³⁺ to detect methanol and hydrocarbon gases, i.e., ethylene, ethane, propane and *iso*-butane. Dy³⁺ is excited by adsorbates produced in a course of catalytic oxidation of these gases. The γ -Al₂O₃:Dy³⁺ CTL-based sensor is sensitive for the wide concentration range from 0.2 to 1000 ppm for *iso*-butane and propane, and has linear characteristics on gas concentrations lower than 10 ppm.

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