Detection of Organic Molecules Dissolved in Water Using a γ-Al_2O_3 Chemiluminescence-Based Sensor

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A new method is proposed for recognizing organic molecules dissolved in water using a chemiluminescence-based sensor made with a γ-Al_2O_3 catalyst. When a mixture of air and organic molecules, *e.g.* ethanol and acetone vaporized from a solution, flows around the sensor, chemiluminescence (CL) is emitted during its catalytic oxidation. The CL spectra consist of subbands peaking at the same wavelengths independent of the type of vapors. The peak wavelengths of these subbands are the same as those for CL with a $CaCO_3$ catalyst. The relative CL intensity of each band, however, depends on the type of the vapor and the temperature of the sensor. This implies that CL originates in the same kinds of luminous species produced during the course of catalytic oxidation. By keeping a sample gas around the sensor in a state of laminar flow and by keeping the catalytic oxidation on the sensor under the diffusion-controlled condition, the CL intensity becomes stable and reproducible. The CL intensity is proportional to the concentration of these organic vapors in the gas phase within the concentration range of from 1 – 500 ppm.

Keywords Chemiluminescence, sensor, catalytic oxidation, organic molecules, aluminum oxide

Chemiluminescence measurement is a very useful method for detecting molecules. This method has high sensitivity, good reproducibility and selectivity, quick response and good linearity over a wide concentration region. However, it is not convenient for continuous and long-term detection, because a supply of reactants to produce luminescent species through a chemical reaction is required. Although many investigations have attempted to improve these disadvantages since 1960[1–4], a long-term stability of the sensitivity has hardly been attained. A new possibility of a CL-based sensor which does not require a supply of reactants was proposed by Breysse *et al*. in 1976.[5] They observed CL during the catalytic oxidation of carbon monoxide on a thoria surface. In 1990, we found that CL is observed during the catalytic oxidation of organic vapors on an alumina surface.[7] These phenomena can be applied to CL-based sensors. Various methods to detect organic vapors in air have been reported elsewhere.[8–11] In this paper, we deal with a method used to detect organic molecules, *e.g.* acetone and ethanol, dissolved in water using this sensor. We will describe the elementary working mechanism of the sensor and its working condition under which the response is quick and stable.

Experimental

Figure 1 shows a schematic diagram of the measuring system for a CL-based sensor. The CL-based sensor is made of a sintered layer of γ-Al_2O_3 powder with a thickness of 0.5 mm. The pasty mixture of the powder and aluminum nitrate solution of 2 M was laid on a ceramic substrate (3 mm×1.5 mm), and then heated at 900˚C for 2 h. The sensor was heated by an electric heater made of Pt film laid on the reverse side of the substrate. The sensor was placed in a quartz tube having two bundles of Teflon tubes of 1 mm in diameter at both ends of the tube in order to keep the movement of the gas around the sensor in a laminar flow. A sample solution containing organic molecules was placed in a vaporizer kept at a constant temperature. The vapor was mixed with synthesized air (a mixture of 21% oxygen and 79% nitrogen). The mixed gas at atmospheric pressure flowed through the quartz tube and was removed by a diaphragm pump. The mean-flow velocity of the sample gas in the tube ($\bar{v}$) was controlled by a mass-flow controller. The chemiluminescence from the sensor was measured by a photomultiplier through optical filters using a photon-counting technique. For the CL spectrum measurements, a spectrometer was used instead of these filters. The CL intensity at each wavelength was measured at a resolution of 10 nm. The concentration of the organic molecules in the mixed gas was monitored by a mass spectrometer through a differential evacuating system. The results of a catalytic reaction on the sensor were also detected by the mass spectrometer.

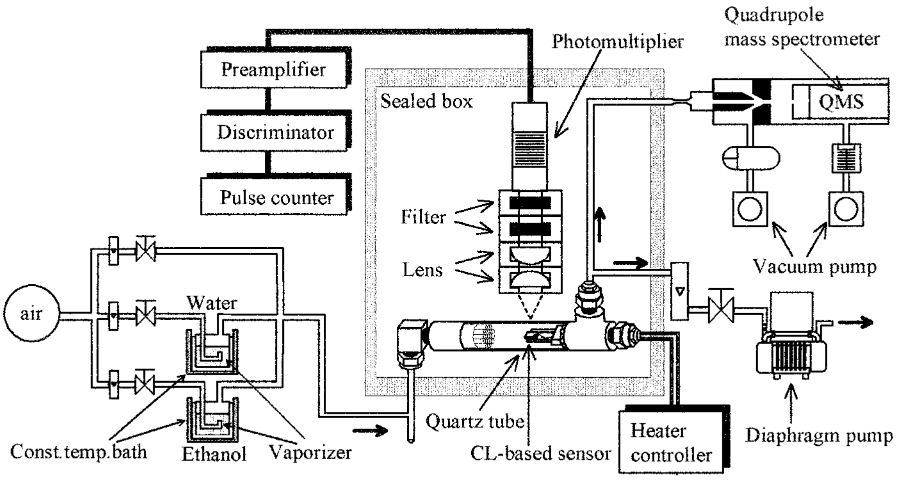

Fig. 1 Schematic diagram of the measuring system for examining the CL-based sensor.

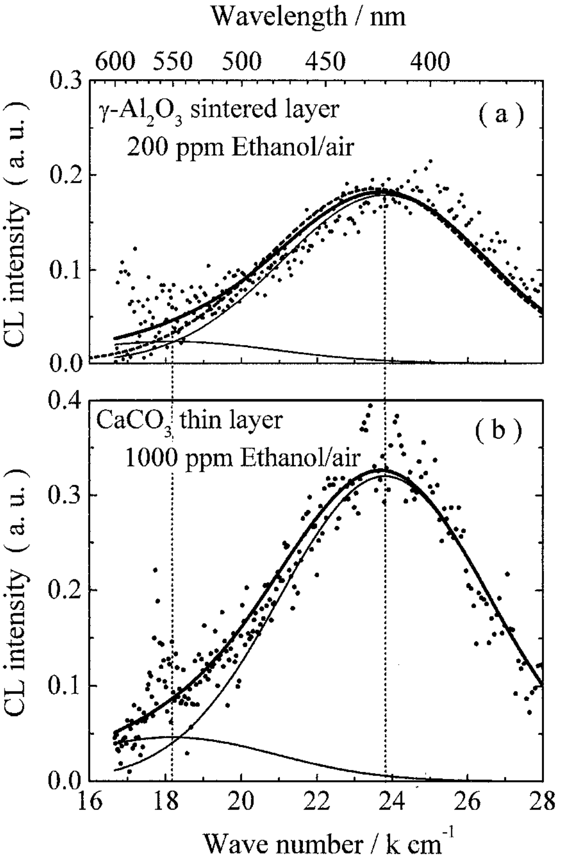

Fig. 2 CL spectra in air containing ethanol vapor for (a) γ-Al_2O_3 and (b) $CaCO_3$ catalysts at 450°C. The thin curves show subbands and the bold curve denotes their sum.

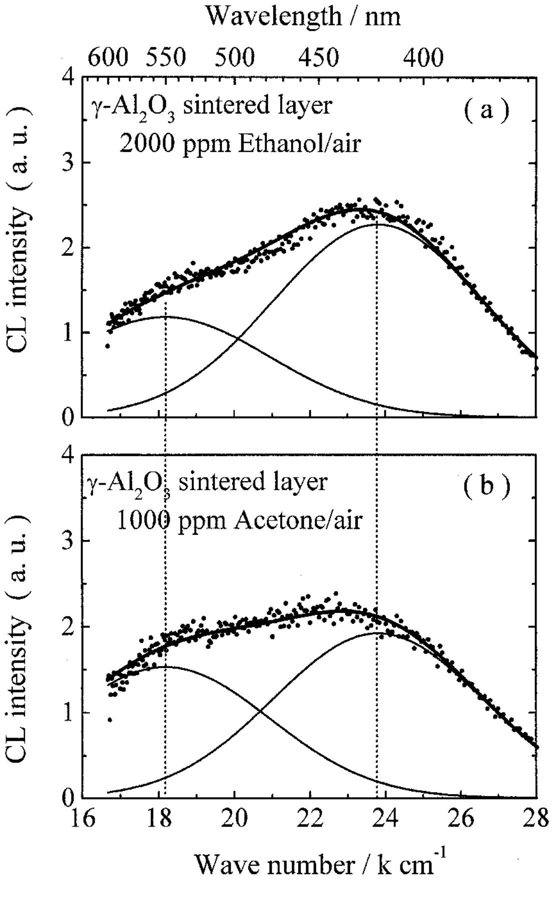

Fig. 3 CL spectra in air containing (a) ethanol vapor of 2000 ppm and (b) acetone vapor of 1000 ppm for the γ-Al_2O_3 catalyst at 450°C. The thin curves show subbands and the bold curve denotes their sum.

Results

CL spectra of the sensor

The CL spectra in air containing ethanol vapor was measured using a layer of a different catalyst. The dots in Figs. 2 (a) and (b) show the CL spectra for (a) the sintered layer of γ-Al_2O_3 and (b) the thin layer of $CaCO_3$ powder. These CL spectra have a peak at about 420 nm. Assuming Gaussian line-shapes, we converted these spectra into subbands peaking at 420 nm and 550 nm by a peak-fitting technique. The thin curves denote the resolved subbands, and the bold curve denotes their sum. The peak-wavelengths of these subbands do not depend on the type of catalyst.

Figures 3 (a) and (b) show the CL spectra for the sintered layer of $\gamma\text{-Al}_2\text{O}_3$ in a gas containing (a) ethanol vapor of 2000 ppm and (b) acetone vapor of 1000 ppm in air. We could also convert these spectra into the same subbands by the peak-fitting technique. The relative peak height of the subbands depends on the type of organic vapor. In the following experiments, the CL intensity was observed using bandpass interference filters having wavelengths between 430 and 470 nm.

Working temperature of the sensor

Carbon dioxide (CO_2) is produced by the catalytic oxidation of ethanol and acetone. Therefore, the relative partial pressure of the gas flowing out through the sensor (P_{CO2}) is an index of the rate of the catalytic oxidation. Figures 4 (a) and (b) show the temperature dependence of the CL intensity between 430 – 470 nm (curve 1) and P_{CO2} (curve 2) in air containing (a) 1500 ppm ethanol and (b) 500 ppm acetone, respectively. As shown by the two curves (2 in both figures), the pressure (P_{CO2}) increases exponentially along with an increase in the temperature below the critical temperature (T_c). It is inclined to saturate above T_c. Such characteristics of the catalytic reaction rate are well known as a reaction under the reaction-controlled condition (the low-temperature region) and under the diffusion-controlled condition (the high-temperature region). That is, the former is the region where the total rate of the catalytic oxidation (r_t) is controlled by the rate of the surface oxidation of the adsorbates on a catalyst (r_r). The latter is the region where r_t is controlled by the rate of diffusion of combustible gas and/or oxygen from the gas phase to the surface of the catalyst (r_d).

The critical temperature (T_c) for the oxidation of 1500 ppm ethanol is 425˚C as shown in Fig. 4(a). The reproducibility of the CL intensity for changes in the ethanol concentration in air was measured at 550 and 350˚C (Figs. 5 (a) and (b), respectively). They correspond to the temperatures under the diffusion-controlled and reaction-controlled conditions, respectively. The CL intensity during injection of ethanol vapor of 1500 ppm into ambient air was stable and reproducible at 550˚C, and was not reproducible at 350 ˚C.

Concentration and flow velocity of gas

It is well known that in catalytic oxidation the critical temperature (T_c) is affected by the flow velocity around the catalyst and by the concentration of the combustible gas. The CL intensity between 430 – 470 nm at 450˚C was measured as functions of the ethanol concentration in gas C_E (Fig. 6 (a)) and the mean flow velocity of the gas around the sensor ($\bar{v}$) (Fig. 6 (b)). The CL intensity is proportional to C_E over a wide concentration range of between 1 and 500 ppm. The CL intensity depends on the square root of $\bar{v}$ at a concentration range lower than 500 ppm, but hardly depends on $\bar{v}$ at higher than 500 ppm, as shown in Fig. 6 (b).

The CL intensity in an atmosphere containing water vapor

The CL intensity was measured for the vapors of ethanol or acetone evaporated from the sample water including various concentrations of these organic molecules. To vaporize these organic molecules in water, air of 500 ml/min flowed through the vaporizer, which was kept at 20˚C, as shown in Fig. 1. The concentration dependence of the CL intensity is shown in Fig. 7. The CL intensity is not proportional to the concentration of organic molecules in water. The mass-spectrum measurements showed that the concentration of organic

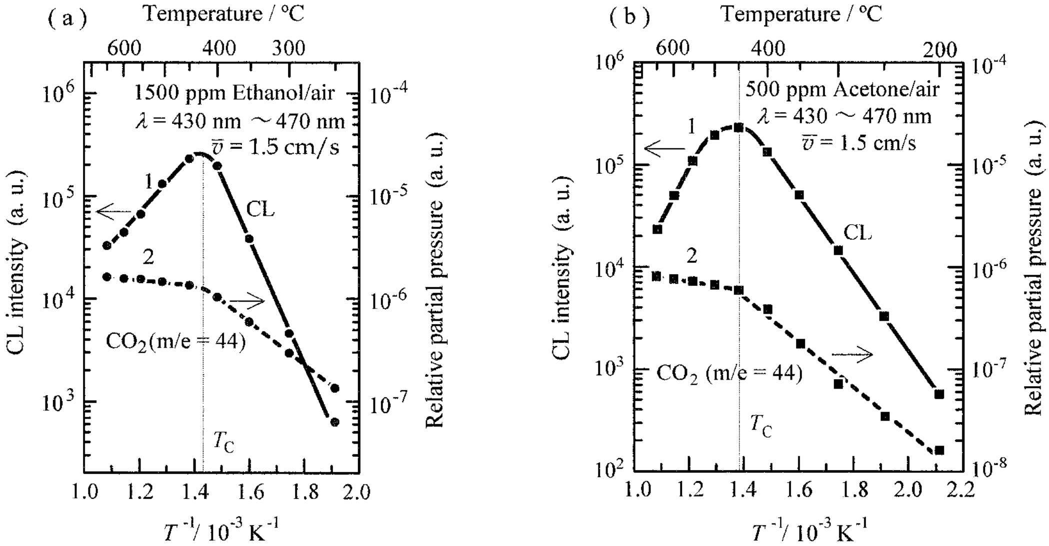

Fig. 4 Temperature dependences of the CL intensity and the partial pressure of the reaction product (CO_2) by the catalytic oxidation of (a) ethanol and (b) acetone vapor on a $\gamma\text{-Al}_2\text{O}_3$ sintered layer.

molecules in gas phase was not proportional to that in the liquid phase. Furthermore, the effect of coexisting water vapor of the higher concentration should be studied further.

To investigate this effect, we measured the response of CL to the injection of ethanol vapor into an air atmosphere containing various concentrations of water vapor. The result is shown in Fig. 8. The CL intensity is reduced by the coexistence of water vapor. Although the CL intensity corresponds to the concentration of ethanol vapor in dry air, an overshoot in the CL response is observed in an atmosphere containing higher concentrations of water vapor. Even under such atmospheres, a stable CL intensity is obtained within 1 min after the injection of ethanol vapor.

Discussion

Based on various observations of the oxidation of carbon monoxide on ThO_2, Claudel *et al.*[6] have presented a mechanism of luminescence emission during catalytic oxidation. They concluded that hole-trapped surface states are produced by the chemisorption of CO, and that electron-trapped surface states are produced by the chemisorption of O on ThO_2. Carbon dioxide bound to an exciton is formed during the course of a surface reaction between these chemisorbed CO and O. The desorption of CO_2 is accompanied by annihilation of the exciton, *i.e.*, by the emission of the corresponding quantum.

This, however, may not be the case of our observations of the CL emission by the catalytic oxidation of ethanol or acetone. If surface states are produced by chemisorption on the catalyst surface, their energy levels must depend on the composition and crystal structure of the catalyst. Therefore, the CL spectrum must depend on the type of catalyst. As shown in Figs. 2 (a) and (b), the subbands contained in the CL spectra emitted by the catalytic oxidation of ethanol have the same peak wavelengths independent of the type of the catalysts of γ-Al_2O_3 and $CaCO_3$. This implies that CL originates in excited molecules, which may be produced during some intermediate steps of the catalytic oxidation. In fact, the profile of the 420-nm band coincided with the CL spectrum observed during the oxidation of ethylene by ozone in the gas phase (the broken line in Fig. 2 (a)). The luminous species is excited formaldehyde in this case[12], and it is well known that formaldehyde is produced during the course of the catalytic oxidation of alcohol. The luminous species of the 550-nm band, however, is unknown.

For the CL spectra, a more interesting result is shown in Figs. 3 (a) and (b). The CL spectra for ethanol and acetone consist of subbands peaking at the same wavelengths. This implies that the same kinds of luminous species are produced during the course of the catalytic oxidation of ethanol or acetone. Because of the difference in the reaction processes to produce them, the amount of each kind of luminous species which creates the CL subbands at different wavelengths may differ from each other, depending on the type of organic molecule.

Since the reaction process is characterized by the activation energy, the difference in the reaction processes can be confirmed by the temperature dependence of the CL intensity. As shown in Figs. 4 (a) and (b), the chemiluminescence by ethanol and acetone shows different activation energies of 0.97 and 0.76 eV, respectively, at the reaction control region below approximately 400°C. Although the detailed reaction process is unknown, these results support the idea that the same luminous species are produced through different reaction process by the oxidation of ethanol and acetone, respectively.

As is well known in catalytic oxidation, the diffusion-controlled region is characterized by the region where the reaction rate does not depend greatly on the temperature. At temperatures above T_c, the surface reaction rate (r_r) exceeds the diffusion rate of gas molecules on the catalyst surface (r_d). In this case, the total reaction rate (r_t) is controlled by r_d, which depends slightly on the temperature. The rate r_t is stable because r_d is determined only by diffusion characteristics of the gases. Therefore, one of the necessary conditions to keep the CL intensity stable is to keep the catalytic oxidation stable under the diffusion-controlled condition. In fact, a good reproducibility of CL is obtained in the

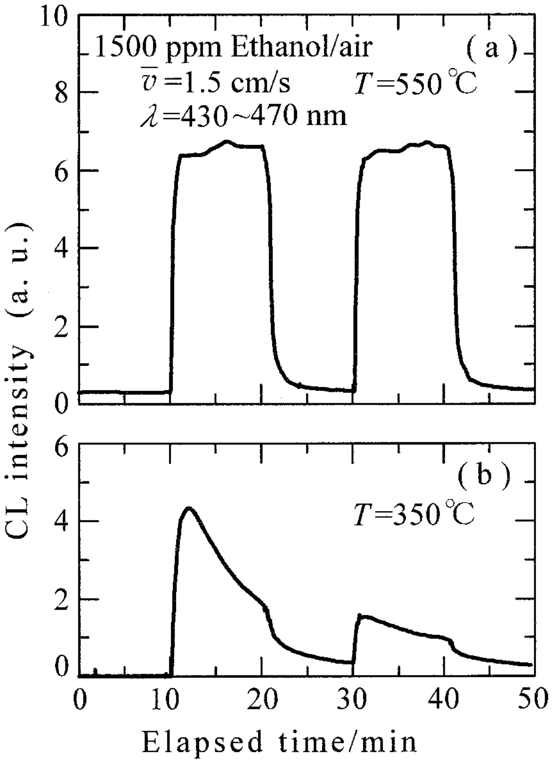

Fig. 5 CL intensity during the injection of ethanol vapor of 1500 ppm into an ambient air atmosphere of a γ-Al_2O_3 sintered layer at (a) 550 and (b) 350°C.

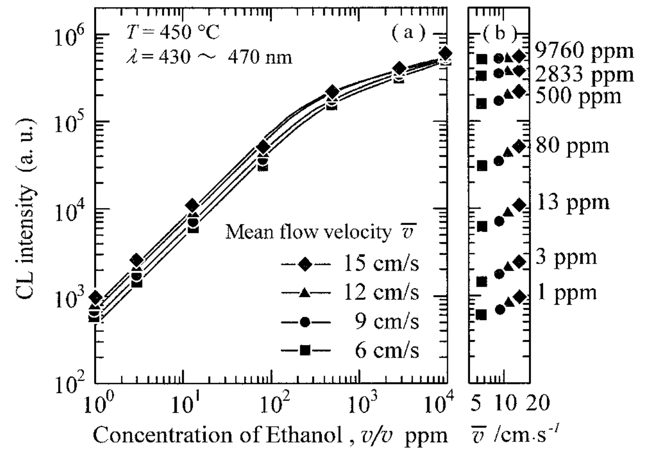

Fig. 6 CL intensity on a γ-Al_2O_3 sintered layer (a) as a function of the ethanol concentration and (b) as a function of the mean-flow velocity.

diffusion-controlled region, as shown in Fig. 5 (a).

It is well known in the theory of flow-dynamics about diffusion in the boundary-layer in a laminar flow that the transportation-rate of a certain molecule by diffusion from the gas phase to a solid surface is proportional to the square root of the flow-velocity ($\bar{v}$) of the gas. Therefore, it can be confirmed directly by the flow-rate dependence of the CL intensity that the sensor is working under the diffusion-controlled condition or not. As shown in Fig. 6 (b), the CL intensity depends on the square root of $\bar{v}$ at the concentrations below 500 ppm. In this diffusion-controlled region, the CL intensity is proportional to the concentration of the ethanol vapor (C_E), as shown in Fig. 6 (a).

The diffusion-rate of ethanol r_d increases as the concentration of ethanol increases, and it will exceed r_r over a certain critical concentration (C_c). Therefore, the reaction changes from the diffusion-controlled condition to the reaction-controlled condition along with an increase in the concentration over C_c of 500 ppm. In fact, in the region where C_E is over 2833 ppm, the CL intensity minimally depends on $\bar{v}$. The reaction may be under the reaction-controlled condition. As shown in Fig. 6(a), the concentration dependence of the CL intensity becomes sub-linear in this region. The reaction to produce a luminous species is suppressed under such conditions. Although, the reaction process is yet unknown, it was found phenomenologically that the luminescent reaction is included in the course of catalytic oxidation, and is strongly affected by the rate-determining step of the total oxidation. The stable and precise working condition of the CL-based sensor is realized under the diffusion-controlled condition of catalytic oxidation.

In the detection of volatile organic molecules in water, the purge-trap method has generally been used. The purged organic molecules from the sample water are condensed in a trap-tube, and are then dehydrated by dry gas. Finally, the thermally desorbed gas from the trap is measured by gas chromatography. The CL-based sensor, which has high-sensitivity and linear characteristics, as shown in Fig. 6(a), is useful as a convenient detector for gas chromatography. Furthermore, Figs. 3 (a) and (b) show that the CL-based sensor can discriminate the type of organic molecules by a spectroscopic measurement of CL.[11] The analytical detection of gases containing two types of organic molecules is also possible.[10] This can be applied for the simple recognition of organic molecules without using a gas chromatograph.

As shown in Fig. 7, a more simple and continuous monitoring of organic molecules in water was tested. We can continuously measure organic molecules by adopting a sampling system of water into the vaporizer. This system can be applied for the continuous monitoring of organic molecules in a manufacturing process. However, the sensitivity of the CL-based sensor is reduced with the coexistence of water vapor, as shown in Fig. 8. The CL intensities of the 420- and 550-nm bands were reduced at a similar ratio. The water vapor may act as a quencher at the luminous reaction process, because the mass spectrum measurement of P_{CO2} showed that the rate of the total oxidation was scarcely affected by water. Therefore, this method is more effective for the detection of organic molecules in a vaporized mixture which can be dehumidified by means of a cold trap or water-absorbing reagents.

One of the advantages of this method using the CL-based sensor for molecular recognition is its stability. Because the oxidation process is at the surface of the sensor, the detecting molecules or other contaminating molecules are oxidized and are desorbed from the sensor surface. Furthermore, the sensor has long-term sta-

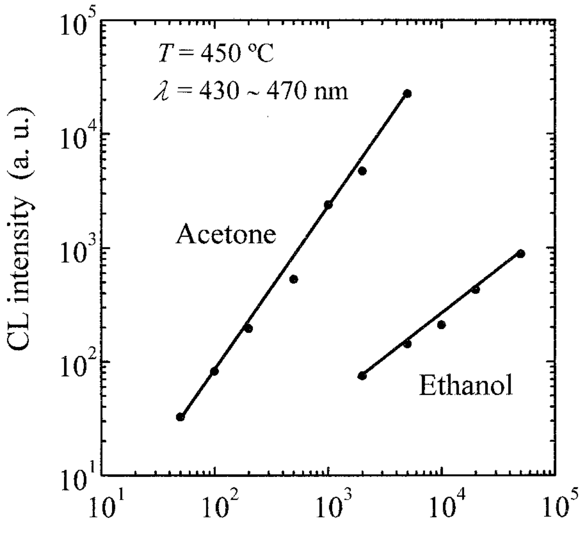

Fig. 7 CL intensity on a γ-Al_2O_3 sintered layer as a function of the concentration of ethanol and acetone dissolved in water.

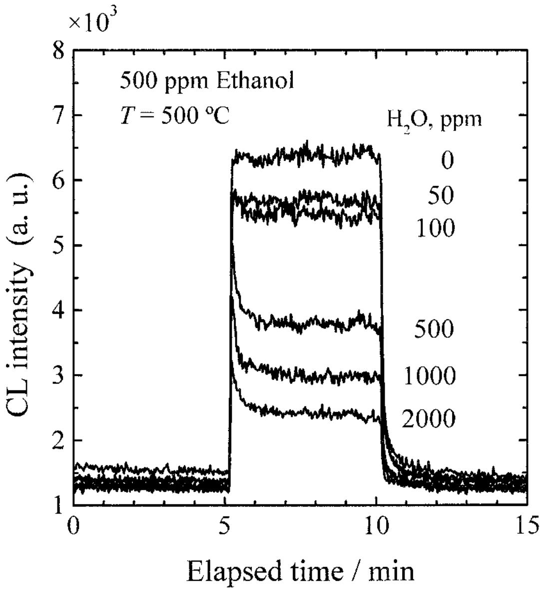

Fig. 8 Response of the CL intensity on a γ-Al_2O_3 sintered layer to the injection of ethanol vapor of 500 ppm into air atmosphere containing various concentrations of water vapor.

bility because it is used under diffusion-controlled conditions where the total reaction rate is governed only by the rate of diffusion. Another advantage is its convenience, in that it works without any supply gas. It is possible to use oxygen in air as an oxidizing gas for the catalytic oxidation of organic molecules. Although the analytical characteristics of this sensor are presently limited, they will be improved in the future by investigating various catalysts for oxidation accompanied by CL emission.

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