REDUCTION OF VOLATILE ORGANIC COMPOUNDS USING PHOTOCATALYSTS ACTIVATED BY BLUE LED

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The effective utilisation of solar radiation requires the development of novel photocatalysts activated by visible-light. Activity tests of toluene decomposition were carried out in the presence of modified titanium dioxide photocatalysts in which some oxygen ions were substituted by sulfur. The elimination of toluene after 1 hour irradiation of the photocatalysts by a pulsed blue LED yielded 44 percent elimination. Pretreatment in which S-doped TiO₂ was irradiated by UV for 1 hour prior to the activity test was effective in decomposing acetaldehyde, even under a pulsed green LED irradiation.

Keywords: Photocatalysts; VOCs; LEDs; visible-lights.

1. Introduction

Photocatalysts decompose some organic compounds on a surface when the catalyst is irradiated with UV light. Research by the Tokushima Prefectural Industrial Technology Center found that the photocatalytic decomposition of acetaldehyde by titanium dioxide under pulsed UV-LED irradiation (50% duty ratio with pulse period of 1ms) showed the same yield as that under continuous UV-LED irradiation, and was especially effective in the decomposition of acetaldehyde at low concentration[1,2]. UV-LEDs are currently expensive but may enable the construction of some compact, high efficiency devices. Recently, much attention has been paid to visible-light-driven photocatalysts from the viewpoint of effective use of sunlight. In this study, oxygen in titanium dioxide photocatalyst was partly substituted by sulfur to improve activation by visible-light, and

activity tests of decomposition of toluene and acetaldehyde, one of the volatile organic compounds (VOCs), were performed using pulsed or continuous blue and green LED irradiations.

2. Experimental

Commercially available titanium dioxide ST-01(Ishihara Sangyo) and the thiourea (typically TiO_2 : thiourea = 1:1 in molar ratio) were mixed[3], and calcined at 400°C for 3 hours so that some oxygens were substituted by sulfurs and the resultant S- TiO_2 is subject to testing of activity with visible light. After the catalyst was mixed with water in a Petri dish to make a slurry, it was dried at 60°C . The dish containing the powder was put in a sampling bag, the inside of which was filled with toluene or acetaldehyde. The bag was left in a dark room for half a day to reach adsorption equilibrium. The continuous or pulsed irradiation by blue and green LEDs (manufactured by Nichia Corporation) was applied from the upper part of the bag (Fig.1), controlling the pulse width and the duty cycle (lighting time/ pulse period). The time evolution of the gas concentration in the bag was calculated from the initial and final concentrations. For reference, S-doped TiO_2 irradiated by UV for 1 hour prior to the test was also prepared, to decompose previously-adsorbed VOCs on the TiO_2 surface [4].

Fig.1 Light LED visible and experiment device chart of photocatalyst.

3. Results and discussions

3.1 Photocatalytic activity against toluene

Applying continuous irradiation by using a green LED (wavelength 520nm), or a blue

Fig.2. Difference of removal efficiency of toluene using green and blue LEDs, respectively.

LED (wavelength 470nm), to the sample, was carried out to assess activity against 100ppm of toluene as the initial concentration. For the green LED, the toluene was only slightly removed, regardless of irradiation time. In contrast, for the blue LED, decomposition efficiency for toluene reached 50% after five hours, but decreased rapidly with elapsed time (Fig.2).

To confirm effectiveness of the pulsed irradiation for the photocatalytic decomposition, the pulsed blue LED irradiation (50% duty cycle and 1000lx in illuminance with pulse period 1ms) was applied to 7ppm of toluene as the initial concentration. The elimination ratio after 1 hour reached 44% at maximum (Fig.3).

Fig.3. Removal efficiency of toluene when duty ratio applied was 50%.

Figure 4 shows the removal efficiency of 11ppm of toluene under similarly controlled blue LED pulse irradiation (except that a 20% duty cycle applied). The low concentration toluene could be removed under the pulsed irradiation with small power consumption. Though toluene is reported to be hard to decompose [5], the visible-light-driven titanium dioxides were activated under an illuminance of as low as 1000lx of the blue LED. As the illuminance at workspaces in offices is around 1000lx, this result suggests the possibility of photocatalytic decomposition of VOCs using TiO_2 under domestic lighting.

Fig.4. Removal efficiency of toluene when duty ratio applied was 20%.

3.2 The schematic model of decomposition and adsorption when continuous and pulsed LED irradiation.

Fig.5. Proposed scheme of decomposition and adsorption mechanisms of VOCs under a continuous (left) and a pulsed (right) LED irradiations.

In addition, we have proposed decomposition and adsorption mechanisms of VOCs in the presence of continuous and pulsed LED irradiations (Fig.5) [1,2]. During the continuous LED irradiation, adsorption and decomposition of VOCs occurs at the same time. In contrast, when the LEDs are turned off, only adsorption behavior occurs and decomposition no longer takes place. Generation of electron-hole pairs at the catalyst surface no longer occurs in the absence of the irradiation and residual active species such as $O_2^{\cdot -}$ and $OH^{\cdot}$ radicals, which form through reactions between an O_2 molecule and an electron and between a H_2O molecule and a hole, respectively, cause the decomposition of VOCs [6]. The decomposition rate in the absence of the irradiation was thus much lower than that in the presence of irradiation. Thus we propose that the S-doped TiO₂ will have enough time to desorb the decomposition products and to absorb more VOCs in preparation for the next LED irradiations while the LED is turned off.

Wang et al reported [7] photocatalytic decomposition of Reactive Red 22 in aqueous suspension of TiO₂ under a pulsed UV LED irradiation with the pulse width of 0.1s in the duty cycle of 9.1%(=0.1s/1.1s). The apparent rate constants for experiments conducted in pulsed, irradiation were 1.5–2 times lower than for those experiments conducted under continuous irradiation. However, the photons emitted from the LED operated under the pulsed irradiation were 10 times lower than those under continuous irradiation. Therefore, the overall photo efficiency for experiments conducted with the pulsed irradiation was much higher than those for experiments with continuous irradiation.

As a consequence, the pulsed irradiation has a comparable efficiency for removal of VOCs to the continuous irradiation. If the period for irradiation is appropriate against the

timescale for absorption, decomposition and removal behavior, the efficiency will be much improved.

3.3 Photocatalytic Activity against Acetaldehyde

Acetaldehyde is reported to be more easily decomposed than toluene. Fig. 6 shows the results of using blue LED continuous irradiation (illuminance: 1000lx, acetaldehyde of initial concentration: 50ppm). Concentration of acetaldehyde decreased with elapsed time, and five hours later its yield reached 46% at maximum.

Fig.6. Removal efficiency of acetaldehyde under blue LED irradiation.

The effect of the pretreatment of the S-doped TiO_2 on photocatalytic decomposition of acetaldehyde with as high an initial concentration as 500ppm was examined under continuous green LED irradiation. The elimination ratio without the exposure to ultraviolet radiation as the pretreatment was less than 10%. However, the preprocessed sample reached an elimination ratio of 35% after one hour, and showed a five times higher elimination ratio (Fig.7).

Fig.7. Removal efficiency of acetaldehyde by preprocessing photocatalysts.

Impurities on the catalytic surface and the adsorbing species would be removed by preprocessing, that is, the exposure to ultraviolet radiation, and as a result, it is thought that even the green LED irradiation may be able to decompose acetaldehyde adsorbed on the cleaned surface. If the surface was not cleaned by pretreatment, the number of the activesites for adsorbing such VOCs would decrease. When visible LEDs were used as a light source for photocatalysts, such a pretreatment as UV irradiation of the S-doped TiO₂ will improve the efficiency and the decomposition ratio.

4. Conclusions

Pulsed irradiation by visible-light LEDs was as effective in the photocatalytic decomposition of VOCs by S-doped TiO₂ as that of the UV-LEDs previously reported to be effective. Because the pulsed irradiation will lead to a low electric power consumption compared with continuous irradiation, further conservation of energy can be expected.

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