

Titanium Dioxide (TiO₂)-assisted Photocatalytic Degradation of Volatile Organic Compounds at ppb Level

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Titanium dioxide (TiO₂)-assisted photodegradation of volatile organic compounds (VOCs), especially malodorous substances at ppb level in closed air are reported. As target VOCs we selected acetaldehyde, dimethyl disulfide (DMDS), dimethyl sulfide (DMS) and methyl mercaptan, because of their toxicity and unpleasant odor at low concentration in closed air. The initial concentrations were fixed at 0.4–5.0 ppm for acetaldehyde, 0.03 ppm for DMDS and DMS and 0.02 ppm for methyl mercaptan respectively. A blacklight UV-lamp was employed as a light source and the intensity of UV-light was controlled at 1.0 mW/cm² (351 nm). The half life of these odorous substances was from 20 min to 120 min and pseudo-first-order reaction rates were $1.1 \times 10^{-2} \text{ min}^{-1}$ (acetaldehyde), $1.4 \times 10^{-2} \text{ min}^{-1}$ (DMDS), $4.8 \times 10^{-2} \text{ min}^{-1}$ (DMS) and $8.0 \times 10^{-3} \text{ min}^{-1}$ (methyl mercaptan). One of the by-products of TiO₂ photodegradation of acetaldehyde was identified as formaldehyde by liquid chromatography/mass spectrometry (LC/MS). These basic data of TiO₂ photodegradation for odorous substances will be useful for the construction of an air purification system using TiO₂ photodegradation in closed air, for example in living rooms, hospitals and care rooms.

Key words — titanium dioxide-assisted photodegradation, ppb level, malodorous substance

INTRODUCTION

In the atmosphere, especially in indoor air, there are many kinds of volatile organic compounds (VOCs).¹⁾ Though their concentrations are generally at low ppb levels, some of them have a harmful influence on the living environment: for example, the odorous substances which are generated by the biological activity of human beings and other animals; the “sick building” chemicals vaporized from paint and bonds used as building materials.

Titanium dioxide (TiO₂, titania) is well-known as an effective photocatalyst for the degradation of organic compounds because of its characteristic reactive functions such as: using only UV-A (wave-

length of 300–400 nm), which is contained in sunlight its electrons can be excited from the ground state; the reaction using TiO₂ can be promoted at room temperature; TiO₂ can be used for a very long period without loss of activity.²⁾ Generally, the kinetic reaction rate in the atmosphere is much higher than that in water.³⁾ Therefore, the application of TiO₂ photodegradation is promoted in the purifying of the indoor environment.⁴⁾ The effect of TiO₂ has been reported widely and many devices based on it have been sold. On the other hand, most research involves degradation of harmful VOCs by TiO₂ photodegradation only at very high concentration levels, from tens to hundreds ppm.⁵⁾ There are few experimental results,⁶⁾ covering tests at low VOC concentrations. The main reason for this is that the microanalysis of VOCs at sub-ppm level, such as the concentration level of VOC in the living environment, need an exclusive analytical system and a large volume of sample gas. An experimental chamber sufficiently large to sample sufficient volume gas from the inside is necessary and

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must be constructed with inactive inner material in order to prevent wall reactions with the VOCs under investigation.

For the design of an indoor air purifier system, basic data on the reaction rate at actual concentration are needed. In this experiment, typical malodorous substances were chosen as for TiO₂ photodegradation tests. Their properties are as follows: Acetaldehyde is contained in a furniture bond, cigarette smoke and residential wastes, and is known as one of odorous substances which cause the "sick building syndrome." Its threshold concentration for human beings is 0.05 ppm and the World Health Organization regulation value for sick building syndrome is 0.17 ppm.⁷⁾ Dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) are organic sulfuric odorous substances. They are generated from the biological digestion process. Their threshold concentrations for a human being are 0.025 ppm for DMS and 0.029 ppm for DMDS, respectively, and their regulation values in indoor air are set at 0.01 ppm in Japan. The threshold concentration of methyl mercaptan for a human being is 0.02 ppb and much lower than those of DMS and DMDS. The source of methyl mercaptan in the indoor environment is the same as DMS and DMDS.

A number of researchers have pointed out that the effect of TiO₂ photodegradation is not clear for gaseous substances such as VOC and malodorous substances at sub ppm level.⁸⁾ Their opinions are as follows: the number of rarefied VOC molecules arriving at the TiO₂ surface is very few at sub-ppm level, so activated radicals generated by TiO₂ cannot react with VOC molecules sufficiently.

According to our experimental results however, it is clear that VOC at sub ppm level reacts effectively in the TiO₂ photodegradation process. The experimental conditions are: the initial concentra-

tion level of objective VOC is sub-ppm; the UV-A irradiation intensity level and wavelength of TiO₂ photodegradation process are the same as the average sunlight level in Japan; a simple experimental system was constructed to simulate the ordinary living-room environment, so that usual sunlight is irradiated to the surface of the TiO₂ paper immersed in the large and rarefied VOC gas atmosphere.

In this paper, we show the basic data, such as the pseudo-first-order reaction rate by TiO₂ photodegradation for rarefied organic sulfuric compounds and aldehyde as typical odorous substances, experimental methods and by-products of the experiment.

MATERIALS AND METHODS

Schematic diagrams of the photoreactors used in this experiment is shown in Fig. 1.

Two types of reactors were used for this experiment examining the adsorption efficiency of odorous substances. The reactor A (60W × 60D × 60H cm, 216 l) was used for the photodegradation experiments on acetaldehyde, DMS and DMDS. It is made mainly of polyacrylate plate. The reactor A has a UV-lamp, a fan to stir the sample air and a thermometer inside. The reactor B (4.3 l) used for the TiO₂ photodegradation experiments on methyl mercaptan is made of Pyrex glass material with an air tight device, because methyl mercaptan evaporates easily and adsorbs on polyacrylate and metal parts. A UV-lamp was placed outside the reactor B. These reactors were kept at 25°C in an air-conditioned room.

The TiO₂, which was immobilized on a sheet of recycled paper, contained five weight percent anatase type TiO₂ crystal employed in this exper-

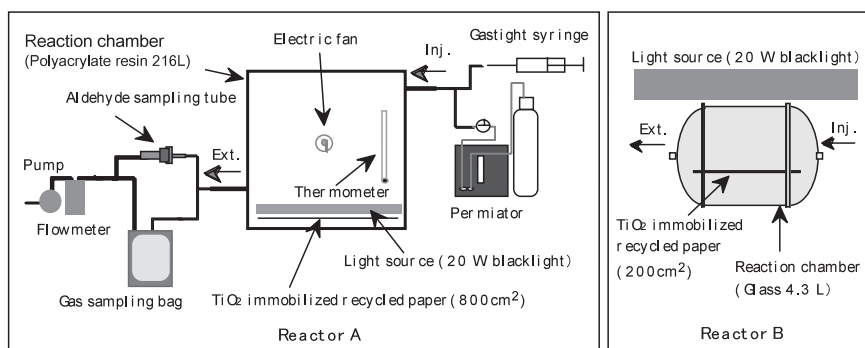


Fig. 1. Scheme of the Reactors and Experimental Systems Employed for TiO₂ Photodegradation of Acetaldehyde, DMS, DMDS and Methyl Mercaptan

iment. The weight for one hundred square centimeters of this paper was 0.95 g. Pieces measuring 800 cm² and 200 cm² of the papers were placed into the reactor A and B, respectively. As the UV-light source of this experiment, a 20-watt black light and an inverter type socket were used. The UV intensity on the surface of TiO₂ paper was controlled at 1.0 mw/cm².

For the preparation of a standard gas, acetaldehyde was purchased from Sigma-Aldrich Co. Ltd. (Tokyo, Japan) DMS and DMDS were purchased from Kanto Kagaku Co. (Tokyo, Japan) and methyl mercaptan was purchased from Taiyo Sanso Co. (Tokyo, Japan) The standard mixtures of DMS, DMDS and methyl mercaptan in air were prepared by introducing appropriate amounts of the standard compounds to glass bottles.

The appropriate volume of these standard gases were injected into the photocatalytic reactor with a gastight syringe; in this way the standard gases were adjusted to the desired initial concentration for each experiment.

The concentration change of the test substances as a function of reaction time was monitored after injecting them into the experimental reactors for two hr in order to confirm the decrease in concentration by adsorption on the surface of TiO₂ paper, metal parts and the inside wall of the reactor. Subsequently, UV irradiation of the TiO₂ paper surface was commenced and the concentration of the test substance was monitored periodically by HPLC and Gas Chromatography-Flame Photometric Detector (GC-FPD) analysis.

Analytical operations for these chemical substances were as follows.

Acetaldehyde: 3 l of sample acetaldehyde gas was taken from the inside of reactor A, and concentrated using a sample tube filled with silica-gel coated with 2,4-dinitrophenylhydrazine. Next, the concentrated 2,4-dinitrophenylhydrazone derivative of acetaldehyde was eluted from the sample tube for aldehyde with 5 ml of acetonitrile. A 20 µl portion of the eluate was injected on to an HPLC-UV. An Octadecyl silica (ODS) analytical column was employed for analysis and the UV-360 nm absorbance was measured and quantified.

DMS and DMDS: 1 l of sample DMS and DMDS sample gas in the reactor A was sampled with a Teflon bag and a suction pump. An appropriate amount (50–200 ml) of the sampled gas was sampled with a gas-tight syringe from the gas bag and injected into a cooled concentration tube, kept

Table 1. HPLC and GC-FPD Conditions

Aldehyde (HPLC)	
HPLC	Agilent 1100 series
Column	Waters SunFire™C ₁₈ , 250 mm × 4.6 mm i.d.
Oven temp.	40°C
Solvent	Acetonitrile/water (3 : 2)
Flow rate	1 ml/min
Detector	UV360 nm
Organic sulfur compounds	
GC-FPD	Agilent 6890 series
Concentration tube temp.	−183°C−125°C/min−70° (3 mins)
Column	25% β, β-ODPN, 3 m × 3 m i.d.
Inj. Temp	130°C
Oven temp	70°C
Carrier	He 60 ml/min
Detector	FPD (H ₂ 90 ml/min, air 70 ml/min)

at −183°C using liquid oxygen. Next, the cooling concentration tube was connected to a GC and heated at a rate of 125°C/min to 70°C. Concentrated DMS and DMDS were introduced to GC-FPD and quantified.

Methyl mercaptan: An appropriate amount of methyl mercaptan sample gas in the reactor B was sampled with a gas-tight syringe directly. The subsequent operations were the same as for DMS and DMDS analytical operations.

HPLC and GC-FPD conditions for the studied substances are shown in Table 1.

RESULTS AND DISCUSSION

Figure 2 shows the change in acetaldehyde concentration with time through the TiO₂ photodegradation process. The initial concentration of acetaldehyde was 0.4 ppm, and was confirmed to be stable for 2 hr before UV irradiation. Though acetaldehyde might adsorb on the inner surface of the reactor and the surface of TiO₂ material, from this result, the amount of adsorbed acetaldehyde reached equilibrium within 2 hr. In the condition of only UV irradiation (without TiO₂ material), the concentration of acetaldehyde hardly changed from the initial concentration after UV irradiation for 420 min. Simultaneously, a small amount of formaldehyde, the by-product of photodegradation of acetaldehyde was generated and then gradually increased. Production of formaldehyde was confirmed by liquid chromatography/mass spectrometry (LC/MS) anal-

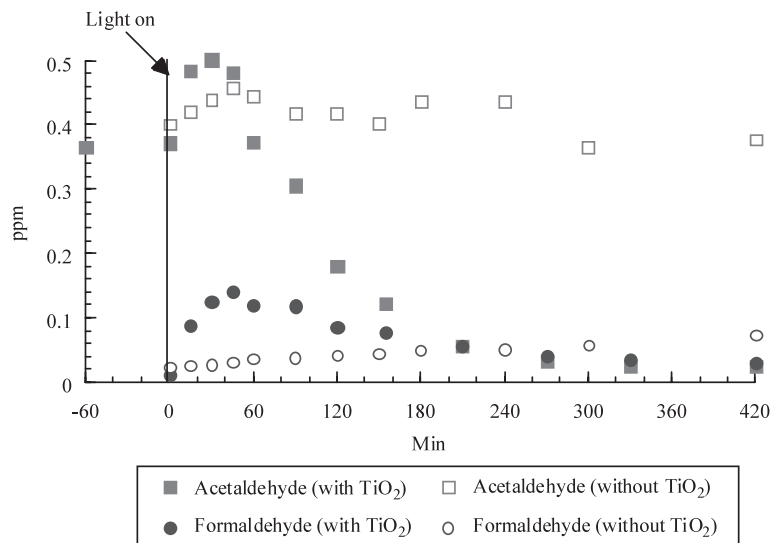


Fig. 2. Time Profile of Acetaldehyde and Formaldehyde during Photolysis in the Presence and Absence of TiO_2 . $[\text{acetaldehyde}]_0 = 0.4 \text{ ppm}$

ysis. Formaldehyde is well-known substance which can cause the sick-building syndrome.

Another report shows that ppm levels of formaldehyde gas can be effectively removed by TiO_2 photodegradation, using a flow-reactor closed air chamber and black light UV-bulb.⁹⁾

On the other hand, the concentration of acetaldehyde began to change immediately, under UV irradiation in the presence of TiO_2 . In the initial period (within 30 min irradiation) the concentration of acetaldehyde increased from 0.4 ppm to 0.5 ppm. Similar results are reported¹⁰⁾ in the experiment of TiO_2 photodegradation for vinyl chloride. The reason for this result may be as follows: the chemical substances adsorbed on the TiO_2 surface and coming to a state of equilibrium in the non-irradiation phase of the experiment are desorbed gradually by lamp heating. After 60 min irradiation, the acetaldehyde concentration began to decrease and became 5% of the initial concentration after 330 min irradiation. Formaldehyde was also generated and then gradually decreased.

The pseudo-first-order reaction constant of acetaldehyde photodegradation was calculated from the time of the highest concentration as a starting point.

The pseudo-first-order reaction constant was calculated by the following equation;

$$kt = -\ln(C/C_0) \quad (1)$$

k : pseudo-first-order rate constant; C : concentration; C_0 : initial concentration; t : reaction time

Table 2. The Pseudo-first-order Reaction Rate of Acetaldehyde in the TiO_2 Photodegradation; Initial Concentration was Varied 0.4 ppm, 1.0 ppm and 5.0 ppm

$[\text{acetaldehyde}]_0$ (ppm)	Pseudo-first-order reaction rate (min^{-1})
0.4	1.0×10^{-2}
1.0	1.1×10^{-2}
5.0	1.1×10^{-2}

The rate constants are shown in Table 2, when the initial concentration was changed from 0.4 ppm to 5.0 ppm. These data remained almost constant when the initial concentration was changed.

The change on time of DMS and DMDS concentration through the TiO_2 photodegradation experiment is shown in Fig. 3. DMS and DMDS were confirmed to be stable for 120 min before UV irradiation. Amounts of DMS and DMDS adsorbed on the inner surface of the batch reactor and TiO_2 material is considered to be negligible and reached equilibrium within a short time; this is also true for acetaldehyde.

Using only UV irradiation, there were only slight changes in the DMS and DMDS concentrations. DMS and DMDS seem to be stable towards UV irradiation of the wavelength used. On the other hand, on UV irradiation with the TiO_2 material, concentrations of DMS and DMDS decreased to half the level of the initial concentration within 20 and 30 min, respectively. Their concentrations decreased to below 5% of the initial concentration after 120 min UV irradiation. The dif-

ference to acetaldehyde is that the concentration of DMS and DMDS did not change in the initial period of the experiment. From this result, it seems that the amounts of these compounds adsorbed on the surface were less than that of acetaldehyde. As by-products of this photodegradation, carbon disulfide was detected. In the first stage of this experiment (within 120 min), the concentration of carbon disulfide was stable at very low concentration. However, in the next step (after 120 min), it increased to 0.02 ppm. The pseudo-first-order reaction rate of DMS and DMDS in this experiment are shown in Table 3.

Methyl mercaptan adsorbed very easily on the

inner surface of the reactor made of acryl board and metal parts. Therefore, the equipment for the experiment was made of glass material that is inactive towards adsorption. The reactor B was used for

Table 3. The Half-life and Pseudo-first-order Reaction Rate of DMS, DMDS and Methyl Mercaptan in the TiO₂ Photodegradation

Compounds	Pseudo-first-order reaction rate (min ⁻¹)
DMS	5.5×10^{-2}
DMDS	4.0×10^{-2}
Methyl mercaptan	8.5×10^{-3}

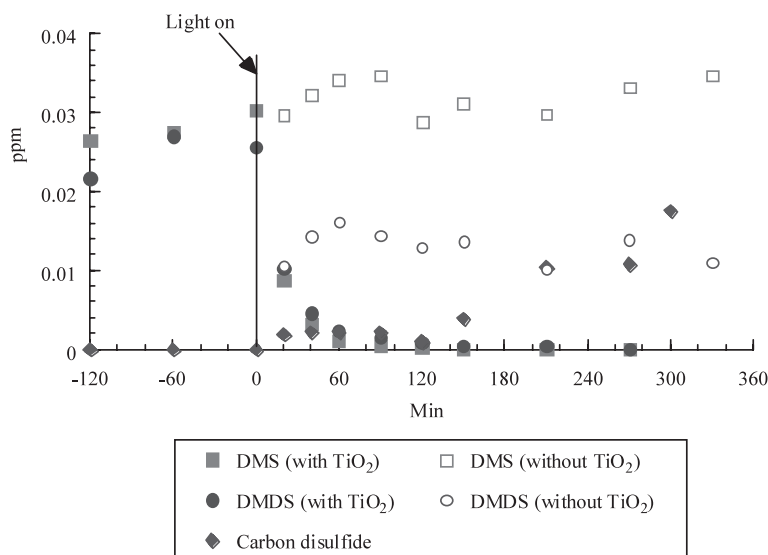


Fig. 3. Time Profile of DMS, DMDS and Carbon Disulfide during Photolysis in the Presence and Absence of TiO₂. [DMS]₀ = 0.03 ppm; [DMDS]₀ = 0.03 ppm

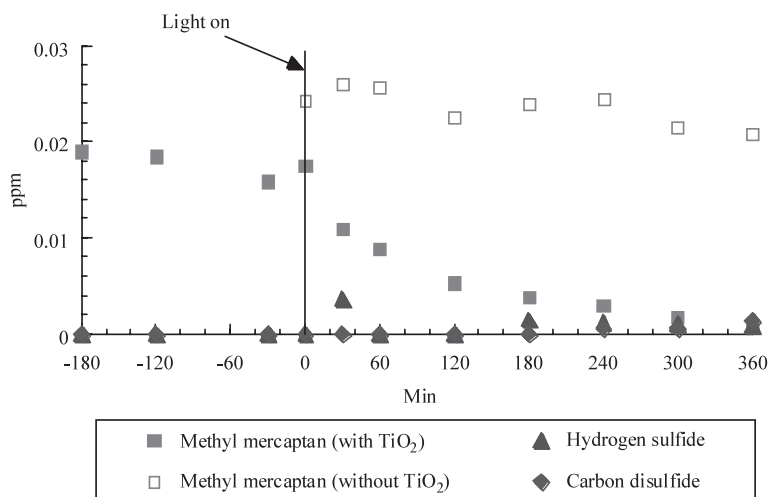


Fig. 4. Time Profile of Methyl Mercaptan, Hydrogen Sulfide and Carbon Disulfide during Photolysis in the Presence and Absence of TiO₂. [Methyl mercaptame]₀ = 0.02 ppm

this experiment. The initial concentration of methyl mercaptan was set at 0.02 ppm. Figure 4 shows the change in the concentration of methyl mercaptan. The concentration of methyl mercaptan was stable at 0.02 ppm for 180 min before UV irradiation. It was confirmed that the amount of methyl mercaptan adsorbed on the surface of TiO₂ material was negligible. The concentration of methyl mercaptan did not change so much during 360 min of UV irradiation without TiO₂ material. However with TiO₂ material, its concentration became half of the initial concentration at 60 min and 90% of methyl mercaptan was decomposed after 300 min UV irradiation. The volume of the reactor B was about 1/50 compared with the reactor A, and the surface area of the paper coated with TiO₂ employed for the reactor B was 1/4 of that used for the reactor A. Consequently, it is difficult to compare the kinetic reaction rates of their photodegradation with TiO₂ directly. However, the photodegradation reaction rate of methyl mercaptan is considered to be much lower than those of acetaldehyde, DMS and DMDS as shown in Table 3.

In the process of TiO₂ photodegradation of methyl mercaptan, hydrogen sulfide and carbon disulfide were detected as by-products. The concentration of hydrogen sulfide decreased with the decrease of methyl mercaptan. By contrast, the concentration of carbon disulfide increased slightly.

In conclusions, in this study, a simple experimental system was employed in order to simulate the action of sunlight in a room on various test chemicals in the presence TiO₂ immobilized paper. From the results it is clear that malodorous test substances at sub-ppm level can be decreased to almost below the threshold concentration by TiO₂ assisted photodegradation.

Using the pseudo-first-order kinetic reaction rate calculated from the experimental results, the TiO₂ photodegradation reaction time needed to remove odorous substances from the air inside the chamber could be estimated.

TiO₂-UV irradiation would be effective at removing odorous substances from domestic living rooms, though it would present a few problems, for example, the reaction rate and the generation of by-products. The concentration of none of the by-products was very low; however a number of them

are more toxic than the initial parent compound. For practical application of the photodegradation method, material(s) which can effectively adsorb these by-products and/or the highly active TiO₂ material should be developed.

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