Photocatalytic Degradation of Formaldehyde and Toluene Mixtures in Air with a Nitrogen-doped TiO_2 Photocatalyst

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Photocatalytic degradation in multiple contaminant system with a nitrogen-doped TiO_2 visible-light photocatalyst was investigated. Formaldehyde and toluene were chosen as components of the contaminant. The degradation rate of toluene was depressed by coexisting formaldehyde, while that of formaldehyde was scarcely affected by coexisting toluene. This phenomenon is attributed to preferential adsorption of formaldehyde on the photocatalyst powder.

Photocatalytic degradation is one of the most promising ways to eliminate the VOCs in indoor air and has been extensively studied.[1–5] However, in many studies, the contaminant is a single component. Actual indoor air is contaminated with multiple components of chemical compounds, such as formaldehyde and toluene. Thus, photocatalytic degradation in multiple contaminant system is important for practical application. Ibusuki et al. have studied photocatalytic oxidation of toluene with/without O_2, NO_2, or H_2O.[6] It was reported that the presence of NO_2 (ca. 40 ppm) enhances the degradation of toluene and formation of CO_2. Sauer et al. and Luo et al. have studied photocatalytic oxidation of toluene and chlorocarbon (trichloroethylene) mixtures in air.[7,8] At high toluene concentration, degradation rate of trichloroethylene was depressed by the coexisting toluene. Ao et al. have studied photocatalytic degradation of formaldehyde in the presence of NO, SO_2, and VOCs (mixture of benzene, toluene, ethylbenzene, and *o*-xylene).[9] The presence of NO enhanced the degradation of formaldehyde, while the presences of SO_2 and VOCs depressed the degradation of formaldehyde. Considering these studies, it is able to say that degradation rate of one contaminant may be enhanced or depressed by coexisting contaminant(s) in multiple contaminant system. In the previous studies, intense ultraviolet light sources and TiO_2 photocatalysts were used. TiO_2 is the most extensively used photocatalyst, however, it utilizes only ultraviolet (UV) light ($\lambda < 380\,\text{nm}$). To make use of interior lighting to eliminate the VOCs in indoor air passively, interior finishing materials coated with photocatalyst having a high activity under visible light ($\lambda > 380\,\text{nm}$) is indispensable. In this study, the photocatalytic degradation in multiple contaminant system with a nitrogen-doped TiO_2 visible-light photocatalyst[10] was thus investigated. Formaldehyde and toluene were chosen as components of the contaminant, because these are major chemical compounds which cause sick building syndrome.

The N-doped TiO_2 visible-light photocatalyst (specific surface area is $280\,\text{m}^2\cdot\text{g}^{-1}$) was synthesized by annealing the powder mixture of anatase TiO_2 (Ishihara Sangyo, ST-01) and urea in air, followed by washing to remove residual urea.[11] A glass plate ($7 \times 7\,\text{cm}^2$) was coated with water suspension of the N-doped TiO_2 powder (0.1 g) and dried as a sample for experiment. Experiments were conducted in a sealed cylindrical reactor (fused silica, $9.2\,\text{cm}\ \phi \times 56\,\text{cm} = 3.7\,\text{dm}^3$) at room temperature ($25 \pm 2\,°\text{C}$). Polluted air was put in the reactor at constant flow rate ($0.1\,\text{dm}^3\cdot\text{min}^{-1}$). In the reactor, pollutant is degraded by a photocatalyst sample under visible-light irradiation. Fluorescent lamp (Toshiba Corp., FL20SW) was used as a light source. To cut the UV light, acrylic board filter was used. The lamp with acrylic board filter emits light of wavelength longer than 370 nm. However, illuminated 6000 lx light contains $2.4\,\mu\text{W}\cdot\text{cm}^{-2}$ UV light (320–400 nm; measured by UVR-2 (Topcon Corp.) UV radiometer with UD36 detector) in this study. Emission spectrum of light source is shown in Figure 1. Detailed description of apparatus for generating polluted inlet air is shown in the previous literature.[12] Formaldehyde was sampled with a DNPH (2,4-dinitrophenylhydrazine) cartridge, and was analyzed by liquid chromatograph (Shimadzu Corp., LP-10Avp). A gas chromatograph mass spectrometer (Shimadzu Corp., VMS-2 VOCs monitoring system) was used to detect toluene. The humidity of inlet gases was controlled to be $50 \pm 5\%$. The inlet and outlet gases of the reactor were sampled. Degradation rate R was calculated from measured concentrations (C_{in} and C_{out}) by the equation $R = (C_{\text{in}} - C_{\text{out}}) \times F \div S$, where F is flow rate and S is sample area. The amounts of adsorbed molecules (formaldehyde and toluene) on the N-doped TiO_2 powder were calculated from differences of concentrations ($C_{\text{in}} - C_{\text{out}}$) in dark conditions.

Figure 2 shows dependence of formaldehyde degradation rate ($R_{\text{F-ALD}}$) on coexisting toluene inlet concentration (C_{TOL}). The rate of formaldehyde was scarcely affected by coexisting toluene. Figure 3 shows dependence of toluene degradation rate (R_{TOL}) on coexisting formaldehyde inlet concentration ($C_{\text{F-ALD}}$). In this case, the rate of toluene was drastically affected by coexisting formaldehyde.

This fact is able to be explained by the following hypothesis. The surface of the N-doped TiO_2 photocatalyst powder in the humid air is hydrophilic. Formaldehyde, which is hydrophilic molecule, is adsorbed sufficiently on the photocatalyst surface, while toluene, which is hydrophobic, is not. The hydrophobic behavior of toluene on the N-doped TiO_2 photocatalyst powder is also reported in the literature.[13] In the multiple contaminant system, formaldehyde is preferentially adsorbed on the surface,

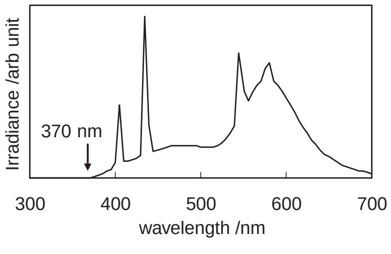

Figure 1. Emission spectrum of light source.

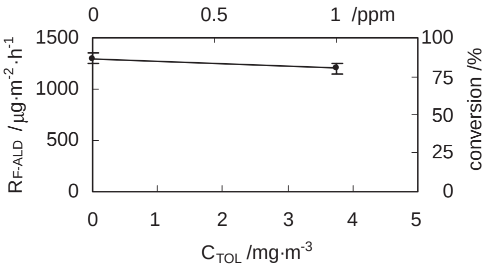

Figure 2. Dependence of formaldehyde degradation rate ($R_{\text{F-ALD}}$) on coexisting toluene inlet concentration (C_{TOL}). Formaldehyde inlet concentration was 1.2 mg·m^{-3} (1 ppm) and flow rate was 0.1 dm^3·min^{-1}. N-doped TiO_2 photocatalyst (0.1 g, 49 cm^2) was illuminated with 6000 lx visible light.

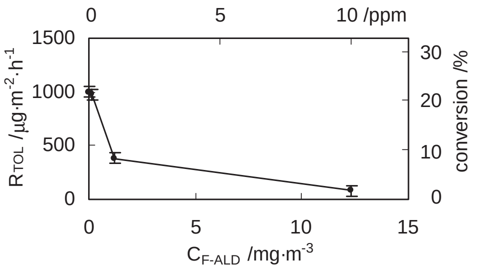

Figure 3. Dependence of toluene degradation rate (R_{TOL}) on coexisting formaldehyde inlet concentration ($C_{\text{F-ALD}}$). Toluene inlet concentration was 3.8 mg·m^{-3} (1 ppm) and flow rate was 0.1 dm^3·min^{-1}. N-doped TiO_2 photocatalyst (0.1 g, 49 cm^2) was illuminated with 6000 lx visible light.

and as a result, adsorption sites for toluene molecule decrease. Thus, the degradation rate of toluene is decreased by coexisting formaldehyde. The amount of adsorbed formaldehyde (inlet gas was 1 ppm formaldehyde only) was measured to be 20 ± 1 μg on the 0.1 g of N-doped TiO_2 powder in dark condition, while adsorbed toluene (inlet gas was 1 ppm toluene only) was below the detection limit (0.05 μg). This result is consistent with the hypothesis that formaldehyde is preferentially adsorbed.

Considering practical indoor use, degradation rates at much lower concentration (0.1 ppm, around the guideline concentration)[14] and at much lower illuminance (150 lx, typical illuminance in indoor lightings) is important. Degradation rates for both formaldehyde and toluene under such experimental conditions are shown in Tables 1 and 2, respectively. It was also found that the rate of formaldehyde was scarcely affected by coexisting toluene, while that of toluene was depressed by coexisting formaldehyde at 150 lx. At the same time, the tendency was not apparent at 1000 lx. This is attributed to the fact that formaldehyde is degraded very rapidly under sufficient illumination, and toluene adsorption is scarcely affected by the coexisting formaldehyde.

Table 1. Dependence of formaldehyde degradation rate ($R_{\text{F-ALD}}$/μg·m^{-2}·h^{-1}) on coexisting toluene inlet concentration (C_{TOL})

C_{TOL}/mg·m^{-3}	0	0.38
150 lx	45 ± 5	56 ± 5
1000 lx	110 ± 5	93 ± 5

[a] Formaldehyde inlet concentration was 0.12 mg·m^{-3} (0.1 ppm) and flow rate was 0.1 dm^3·min^{-1}. N-doped TiO_2 photocatalyst (0.1 g, 49 cm^2) was illuminated with 150 lx or 1000 lx visible light.

Table 2. Dependence of toluene degradation rate (R_{TOL}/μg·m^{-2}·h^{-1}) on coexisting formaldehyde inlet concentration ($C_{\text{F-ALD}}$)

$C_{\text{F-ALD}}$/mg·m^{-3}	0	0.12
150 lx	7 ± 3	0 ± 3
1000 lx	44 ± 3	32 ± 3

[a] Toluene inlet concentration was 0.38 mg·m^{-3} (0.1 ppm) and flow rate was 0.1 dm^3·min^{-1}. N-doped TiO_2 photocatalyst (0.1 g, 49 cm^2) was illuminated with 150 lx or 1000 lx visible light.

It is expected that the same phenomenon occurs when TiO_2 photocatalyst is illuminated by UV light, considering the hypothesis. However, the phenomenon was not observed obviously with TiO_2. This is attributed to the fact that the degradation rate of formaldehyde ($R_{\text{F-ALD}}$) was much higher than that of toluene (R_{TOL}) over UV-illuminated TiO_2, while $R_{\text{F-ALD}}$ was almost equal to R_{TOL} with vis-illuminated N-doped TiO_2. $R_{\text{F-ALD}}$ was measured to be 140 ± 5 μg·m^{-2}·h^{-1} and R_{TOL} was 3 ± 3 μg·m^{-2}·h^{-1} in the present experiment with TiO_2 (Degussa, P25) under UV-light illumination (black light lamp, Toshiba Corp., FL20SBLB, irradiance: 3 μW·cm^{-2}) at low concentrations (0.1 ppm). This result ($R_{\text{F-ALD}}/R_{\text{TOL}} \approx 10^2$ at low concentrations) is consistent with the previous literatures.[2,3]

From the present results, it is concluded that degradation rates of hydrophobic molecules (e.g. toluene) are depressed by coexisting hydrophilic molecules (e.g. aldehydes) when N-doped TiO_2 visible-light photocatalysts are applied to passive purification of indoor air, which is contaminated with multiple chemical compounds at both low concentrations and illuminations.

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14 In Japan, the Ministry of Health, Labour and Welfare specified 13 VOCs as origins of sick building syndrome and announced the guideline on the concentrations of these compounds. The guideline concentration of formaldehyde is 0.1 mg·m^{-3} (0.08 ppm), and that of toluene is 0.26 mg·m^{-3} (0.07 ppm).