



# Degradation of trichloroethylene using highly adsorptive allophane–TiO<sub>2</sub> nanocomposite

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## ABSTRACT

A highly adsorptive allophane–TiO<sub>2</sub> nanocomposite photocatalyst was prepared by dispersing nanoparticles of the natural clay mineral allophane into a titanium alkoxide solution by the sol–gel method. During the photocatalytic degradation of trichloroethylene using the allophane–TiO<sub>2</sub> nanocomposite, emission of the intermediate product, phosgene, was drastically inhibited. Trichloroethylene was transformed into the intermediate products, phosgene and dichloroacetyl chloride, on the TiO<sub>2</sub> during the UV irradiation. These compounds are rapidly adsorbed on the allophane. The compounds then gradually degraded after diffusing to the TiO<sub>2</sub>.

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## 1. Introduction

Photocatalysis is a significantly important technology that is used to degrade harmful organic pollutants. On the other hand, adsorption is also a useful technique for the removal of such chemicals. Natural clay minerals have attracted considerable attention as adsorbents [1–3]. Adsorption is also important in a photocatalytic degradation process by direct hole oxidation. The clay–TiO<sub>2</sub> composites were studied for the effective adsorption and degradation of organic compounds [4–8]. Allophane, a natural clay mineral distributed throughout the world, is a hydrated aluminosilicate (1–2SiO<sub>2</sub>·Al<sub>2</sub>O<sub>3</sub>·5–6H<sub>2</sub>O) having a 3.5–5.0 nm-sized hollow spherical structure with 0.3–0.5 nm-sized defects on its surface [9–13]. The walls of the hollow spheres consist of inner silica and outer alumina layers with a hydroxylated or hydrated surface. Some studies suggest that these surfaces have a significant ability to adsorb ionic or polar pollutants due to their amphoteric ion-exchange activity and high surface area [9,12,14]. Allophane consists of the smallest structural units of all the clay minerals.

Trichloroethylene (TCE) is usually transformed into harmful intermediate products, such as phosgene and dichloroacetyl chloride (DCAC), during its photocatalytic degradation using TiO<sub>2</sub> [15–25]. It has been difficult to completely inhibit the emission of

such compounds using the composites of clay mineral adsorbents and TiO<sub>2</sub> [6–8]. One of the reasons for this is that the particle size of the adsorbents is much larger than that of TiO<sub>2</sub>. The inhibition of the emission of such intermediate products requires controlling the adsorption and photocatalytic reaction fields on the photocatalysts at a nanometer level in order to diffuse such compounds between the fields. The nanocomposite consisting allophane and TiO<sub>2</sub> is expected to effectively adsorb such compounds and degrade TCE without emitting them due to its very small particles having a high surface area. The sol–gel method is valuable for the dispersion of small clay particles into TiO<sub>2</sub> by the addition of the particles into the precursor titanium alkoxide system.

In this study, the nanocomposite photocatalysts consisting of allophane and TiO<sub>2</sub> were prepared from the titanium alkoxide solution dispersing nanoparticles of allophane by a simple sol–gel process. The photocatalytic activity of the nanocomposite for the degradation of TCE was compared to normal TiO<sub>2</sub> and a mixture of allophane and TiO<sub>2</sub>. The degradation of TCE was evaluated by FTIR spectroscopy [15,17,18,21–25].

## 2. Experimental

### 2.1. Materials

Titanium tetraisopropoxide (TTIP), hydrochloric acid (35%), TCE, and ethanol of S reagent grade were obtained from Wako Pure Chemicals. DCAC of reagent grade was obtained from Tokyo Kasei.

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The dry nitrogen gas and dry air gas (ca. nitrogen 79%+oxygen 21%) were obtained from Okaya Sanso. These materials were used without further purification. The water was deionized and distilled (Yamato WG23). Allophane was extracted by the elutriation of Kanuma soil from Tochigi, Japan, as already described [26–28].

## 2.2. Sample preparation

The sol–gel reaction systems were prepared by mixing 6.8 cm<sup>3</sup> of TTIP, 40.0 cm<sup>3</sup> of ethanol, and 1.0 cm<sup>3</sup> of hydrochloric acid. TTIP was dropwise added to the mixture of the other materials in a glove box filled with dry nitrogen gas at ambient temperature. The allophane was dispersed in the sol–gel system in which the Al/Ti ratio was 1/20. This ratio was selected because adding such amount of allophane clearly influenced the photocatalytic activity. The sol–gel systems with and without allophane were agitated by ultrasonication for 3 days. The resulting gel samples were hydrothermally treated at 100 °C, then heated at 400 °C for 3 h.

## 2.3. Characterization of samples

The prepared samples were characterized by XRD analysis using Cu K $\alpha$  radiation (Rigaku RINT2000) and SEM (Hitachi S-4100). The size of the crystallites of each sample was estimated from its full-width at half-maximum of the 25.3° peak in the XRD pattern using Sherrer's equation,  $D = 0.9\lambda/\beta \cos\theta$ . The specific surface areas of the samples were measured by the volumetric gas adsorption method using nitrogen gas (BEL Japan, BELSORP-mini).

The amounts of TCE and DCAC adsorbed on the samples were estimated by gas chromatography–mass spectrometry (Shimadzu GCMS-QP5000). DCAC is a product of the TCE degradation. Allophane of 3.0 mg or each of the other sample of 30 mg was placed in a glass vial. The TCE gas diluted with dry air was injected into the vials in which its concentration was  $3.2 \times 10^{-4}$  mol dm<sup>-3</sup>. Allophane of 1.0 mg or each of the other sample of 10 mg was also placed in other glass vial. The DCAC gas diluted with dry air was injected into the vials in which its concentration was  $3.2 \times 10^{-4}$  mol dm<sup>-3</sup>. The adsorption abilities of the samples for TCE and DCAC were estimated from the concentrations after their adsorption equilibria by GCMS analysis.

## 2.4. Photocatalytic degradation of TCE

The samples of 0.30 g were placed in an infrared cell made of Pyrex glass with KBr single crystals. The TCE gas diluted with dry air was injected into the infrared cell in which its concentration was  $3.2 \times 10^{-4}$  mol dm<sup>-3</sup>. The cell was kept at ambient temperature until the adsorption of TCE was equilibrated. The degradation reaction of the TCE was carried out in the cell by near-UV light irradiation using a 4 W black light bulb (Toshiba FL4BLB) at ambient temperature. The FTIR spectra (Shimadzu FTIR-8300) of the gas phase in the cell were observed as a function of the light irradiation time. The changes in the concentrations of TCE and the products were determined during the TCE degradation using the prepared TiO<sub>2</sub> (Sample T) and allophane–TiO<sub>2</sub> composite (Sample C) and the mixture of allophane and TiO<sub>2</sub> (Al/Ti=1/20) (Sample M). The TCE degradation was repeated six times after each gas replacement.

The changes in the concentration of CO<sub>2</sub> produced from the Samples T, M, and C were observed during the UV irradiation after the fourth TCE degradation in order to examine the degradation of the species adsorbed on the samples.

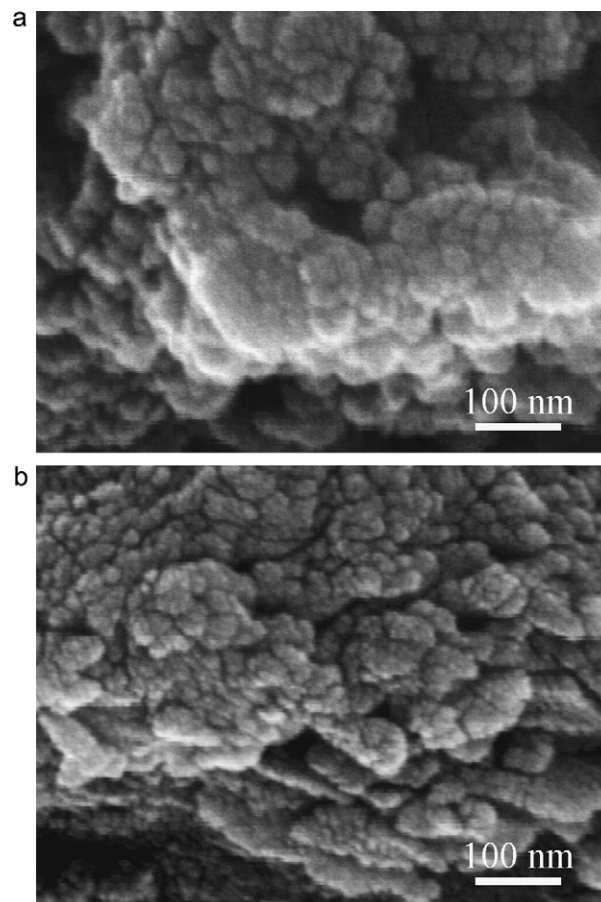


Fig. 1. SEM images of (a) Sample T and (b) Sample C.

## 3. Results and discussion

### 3.1. Characterization of the samples

Fig. 1 shows the SEM images of Samples T and C. Sample T consisted of 20–30 nm-sized particles. Sample C contained the 5–10 nm-sized particles attributed to the allophane. The particle size of TiO<sub>2</sub> in Sample C was also smaller than that in Sample T because the allophane prevented the particle growth of TiO<sub>2</sub>. The EDX analysis revealed the allophane particles were highly dispersed among the TiO<sub>2</sub> particles as previously shown [28].

The anatase and rutile-type crystals were observed in Sample T by XRD analysis. Their crystallite sizes were estimated using Sherrer's equation to be 8.9 nm for the anatase and 7.6 nm for the rutile. Sample C contained 7.0 nm anatase-type crystallites. The samples also consisted of secondary particles. The secondary particles of Sample C should consist of the allophane and TiO<sub>2</sub> nanoparticles.

The specific surface areas of the allophane and Samples T, M, and C were estimated to be 312, 66.0, 90.6, and 95.1 m<sup>2</sup> g<sup>-1</sup>, respectively. The value of the allophane was much greater than that of the TiO<sub>2</sub>. The values of Samples M and C correspond to the sum of the fractional specific surface areas of the allophane and TiO<sub>2</sub>.

### 3.2. Photocatalytic degradation of TCE

The concentration of TCE decreased while those of CO and CO<sub>2</sub> increased due to the UV irradiation during the first photocatalytic degradation of TCE for all the samples. The expected products, phosgene, DCAC, and HCl, were not found in the first run due to adsorption by the TiO<sub>2</sub> or allophane [29]. TCE was not detected

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