



Research Paper

Enhanced photocatalytic activity of titanium dioxide/allophane mixed powder by acid treatment

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ABSTRACT

The TiO₂/allophane mixed powders at various mixing ratios were acid-treated to obtain a highly active photocatalyst. It was found that amorphous silica surrounding TiO₂ particles was formed after acid treatment by selective dissolution of alumina component in the allophane. The photocatalytic activity of the mixed powder, evaluated by the photocatalytic decomposition rate for gaseous acetaldehyde, was improved by the acid treatment when the mixing ratio of allophane was higher than 5 mass% in spite of the decrease of specific surface area (SSA), while that of the pure-TiO₂ powder was decreased maybe because of the increase of Ti³⁺ defects density on its surface. As for the pure-allophane powder, SSA and adsorption rate for acetaldehyde were decreased by acid treatment. In addition, it was found that the acid treatment of allophane was needed to be performed in the presence of TiO₂ to obtain a highly active photocatalyst from the result of the comparative experiments using mixed powder of acid-treated TiO₂ powder and acid-treated allophane powder. Based on these results, it was concluded that the silica-dispersed microstructure of the nanocomposite was suitable for the efficient removal of acetaldehyde.

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1. Introduction

Many studies have been performed on the application of titanium dioxide (TiO₂) photocatalyst to water and air purification because TiO₂ can photodecompose most organic matters under UV irradiation (Fujishima et al., 2008; Kraeutler and Bard, 1978). However, it is widely-accepted that TiO₂ photocatalysis is feasible only for the treatment at low to medium pollutant concentrations because the photocatalytic decomposition rate of TiO₂ is low in many situations. To propagate its practical application, a development of highly active photocatalyst is necessary.

Combination of TiO₂ with adsorbents such as silica, alumina, zeolite (Takeda et al., 1995), activated carbon (Liu et al., 2006), layered double hydroxides (Carja et al., 2010) and hydroxyapatite (Ono et al., 2013), has been adopted to obtain a highly active photocatalyst based on a recognition that photocatalytic reactions occur on TiO₂ surface and then an adsorption property is a significant factor. Among the adsorbents, clays are preferable in terms of low costs and high SSA. Nishikiori et al. (2011) prepared highly adsorptive photocatalyst by sol-gel method using titanium alkoxide solution and allophane which is a very poorly crystalline hydrous aluminosilicate having 3.5–5.0 nm-sized hollow spherical structure (Wada and Wada, 1997). This nanocomposite showed higher rates than a pure TiO₂ powder for the adsorption of intermediate products such as phosgene and dichloroacetyl chloride and for the generation of carbon dioxide in repeated runs of photocatalytic decomposition

of trichloroethylene. They explained that high surface area and high dispersion into TiO₂ of the allophane were the critical factors for the high photocatalytic activity.

On the other hand, it has been reported that the adsorption properties of kaolinite (Okada et al., 1998; Panda et al., 2010) and halloysite (Zhang et al., 2012) were improved by acid treatment. For example, Zhang et al. (2012) demonstrated that the SSA of halloysite was increased from 48 m²/g to 259 m²/g by a treatment with sulfuric acid for 3 h and the acid-treated halloysite showed 4 times larger adsorption capacity for methylene blue dye than the non-treated kaolin. It is considered that the enhanced adsorption capacity was derived from the selective leaching of alumina component to form microporous and/or mesoporous silica structure with high SSA.

In the present study, an allophane powder with high SSA (232 m²/g) was used as a starting material. The allophane was mixed with TiO₂ powder and then it was acid-treated to obtain a highly active photocatalyst by improving the adsorption property of the allophane. Their photocatalytic activities were evaluated by in situ Fourier transform infrared spectroscopy (FTIR) study for the photocatalytic decomposition of gaseous acetaldehyde.

2. Experimental procedure

The TiO₂ powder (5.0 g; Degussa, P25) and allophane powder (Sinagawa Kasei, P-1) at various mass ratios (TiO₂: allophane = 98: 2, 95: 5, and 80: 20) were ultrasonically dispersed in 150 ml distilled water for 30 s. After dried at 110 °C, the powders were mixed and

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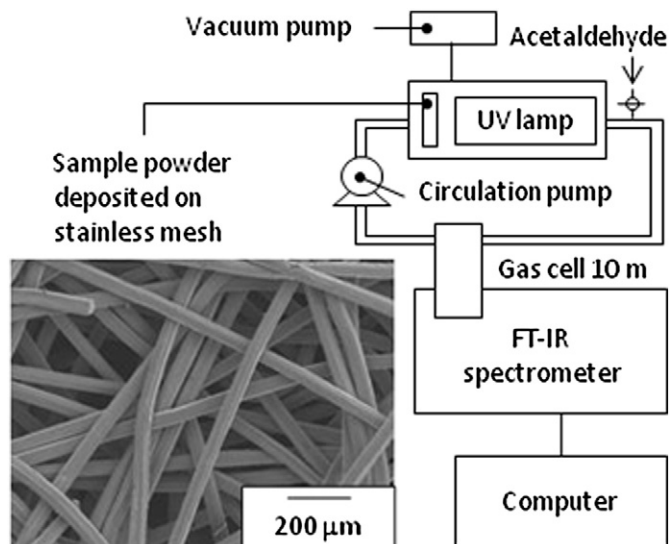


Fig. 1. Schematic illustration for the in situ FTIR equipment used in the experiment of photocatalytic decomposition of gaseous acetaldehyde by photocatalyst powder on stainless mesh. Inset is an SEM image of the stainless mesh.

ground using an alumina mortar. The mixed powder samples were denoted respectively as T98A2, T95A5, and T80A20, according to the mixing ratios. Then the TiO_2 powder, the mixed powders, and the allophane powder, were respectively treated with 1.0 mol/l hydrochloric acid solution (0.6 g/10 ml) in an autoclave reactor at 110 °C for 1.0 h, and centrifuged 3 times with distilled water to rinse the powder surfaces. These resulting samples were denoted as A- TiO_2 , A-T98T2, A-T95A5, A-T80T20, and A-Allophane, respectively.

The powder X-ray diffraction (XRD) measurements were performed using a PHILIPS X'Pert diffractometer with a monochromated $\text{Cu K}\alpha$ radiation (45 kV, 40 mA). The surface areas were measured by a single-point N_2 -BET method (YUASA CHEMBET-3000) using samples dried at 150 °C for 24 h before the measurement. The bulk chemical compositions were determined by X-ray fluorescence (HORIBA XGT-5000). The FTIR spectra of powder samples were measured using JEOL WINSPEC50 FTIR spectrometer equipped with SensIR Durascope ATR accessory at a resolution of 4.0 cm^{-1} . The transmission electron microscope (TEM) images were obtained using HITACHI H-8100 at an acceleration voltage of 200 eV. The electron spin resonance (ESR) spectra were recorded by JEOL RE3X instrument under UV irradiation at 103 K. The density of Ti^{3+} spin in

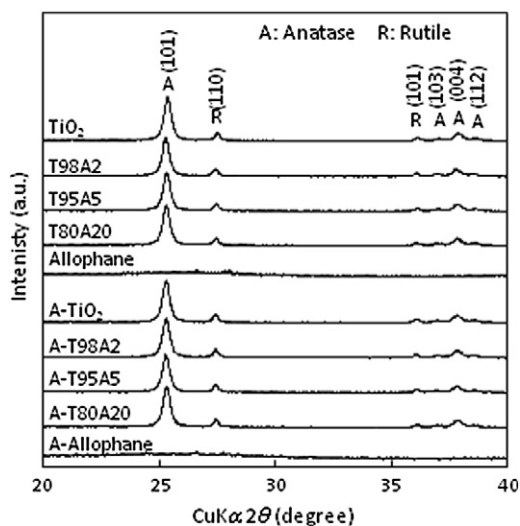


Fig. 2. XRD patterns of the powder samples.

Table 1

FWHM value of (101) anatase peak in XRD pattern, bulk Si/Al and Si/Ti atomic ratios estimated by using peak intensity in XRF study, and specific surface area measured by N_2 -BET method of the powder samples obtained before and after acid treatment.

Sample	XRD FWHM (deg.)	Chemical composition		Surface area (m^2/g)
		Si/Al ratio	Si/Ti ratio	
TiO_2	0.35	–	0.01	42
T98A2	0.35	1.5	0.02	46
T95A5	0.36	1.6	0.04	53
T80A20	0.34	1.4	0.12	72
Allophane	–	1.5	–	232
A- TiO_2	0.36	–	0.01	41
A-T98A2	0.34	No Al peak	0.02	43
A-T95A5	0.34	No Al peak	0.02	48
A-T80A20	0.36	10.3	0.09	61
A-Allophane	–	2.6	–	221

the sample was determined from a peak at $g = 1.991$ (Kumar et al., 2006) obtained by doubly integrating the ESR spectra using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a standard sample (Firsova et al., 2008).

The 0.1 g of the powder sample was deposited on stainless mesh filter of 100 mm by 65 mm (Naslon, Nippon seisen, 50 μm in diameter) by immersing the filter in the powder-dispersed suspension (0.3 g powder/30 ml distilled water) and drying at 110 °C for 10 min. The amount of the sample loaded on the stainless mesh filter was controlled by measuring the changes of the weight of filter sample after the repeated immersing and by adjusting the number of the times of the immersing. The filter sample was set in the reaction chamber (50 l) connected to the FTIR spectrometer (JIR-100, JEOL) as shown in Fig. 1 in a constant temperature and humidity room at 23 °C and 30% RH. After an evacuation, acetaldehyde (40 μl) was injected in the equipment and the air containing acetaldehyde was circulated in the equipment at 17 l/min with a pump at atmospheric pressure. After circulating for 2 h in the dark, the filter sample was irradiated with a 4 W UV (365 nm) lamp at an intensity of $1.0 \text{ mW}/\text{cm}^2$. The changes in the amounts of acetaldehyde, acetic acid, and carbon dioxide gases were examined by measuring the absorbances in IR spectra with a wavenumber resolution of 2.0 cm^{-1} .

3. Results and discussion

3.1. Preparation and characterization

XRD patterns of the starting TiO_2 powder, mixed powders at various mass ratios (T98A2, T95A5, T80A20), and the starting allophane powder

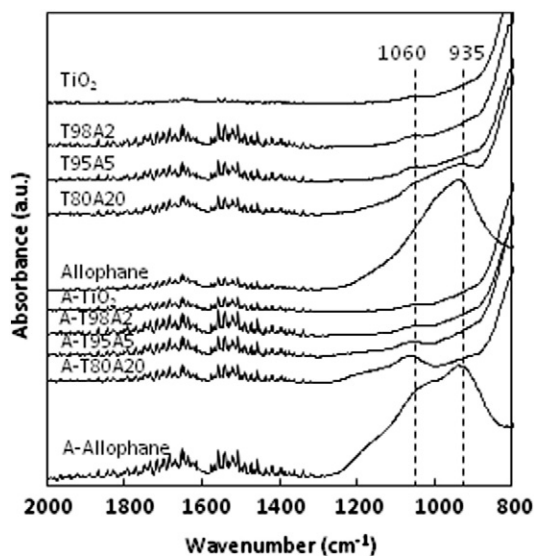


Fig. 3. FTIR spectra of the powder samples.

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