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Visible-light-driven photodegradation of acetaldehyde gas catalyzed by aluminosilicate nanotubes and Cu(II)-grafted TiO_2 composites

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ABSTRACT

Aluminosilicate nanotubes and Cu(II)-grafted TiO_2 composites were prepared, and the acetaldehyde degradation activity of the composites was evaluated at various relative humidities. The aluminosilicate nanotubes were synthesized hydrothermally and characterized by TEM, XRD, ^{27}Al and ^{29}Si NMR, FT-IR, N_2 and water vapor isotherms. Their morphology was nanotubular with 3–5 nm outer diameter, and the specific surface area was 245 m^2/g. The aluminosilicate had a strong affinity for water molecules, and the structure was determined to be an imogolite by ^{27}Al and ^{29}Si NMR. TiO_2 and imogolite composites exhibited higher activity for the photodegradation of acetaldehyde under UV irradiation than TiO_2, but was dependent on the relative humidity. Cu(II)-grafted TiO_2 and imogolite composites exhibited higher activity for the photodegradation of acetaldehyde under visible light irradiation than Cu(II)-grafted TiO_2, and were less affected by the relative humidity. These results show that Cu(II)-grafted TiO_2 - imogolite composites exhibit very efficient absorption and photodecomposition of acetaldehyde in a variety of environments.

1. Introduction

Volatile organic compounds (VOCs) are typical air pollutants mainly emitted from industrial processes and transport vehicles. These cause various environmental problems and have adverse effects on human beings. The removal method of VOCs from air has been attempted using physical, chemical, and biological techniques [1–3], of which activated carbon adsorption is the most widely studied and used [4–10]. However, this method simply transfers organics from the gas to the solid phase, and increases the environmental load because of the need to dispose of the activated carbon containing adsorbed VOCs. A method which can completely decompose or remove VOCs is needed.

Titanium dioxide (TiO_2) is a well-known efficient photocatalyst [11]. TiO_2 is activated by irradiation with ultraviolet (UV) light, generating electron–hole pairs which reduce and oxidize adsorbates on the surface, thereby producing radical species, such as OH radicals and $O_2{}^-$. These radicals are strong oxidizing agents and can decompose most organic compounds [12–17] and bacteria [18–22]. Many studies have been conducted on the application of TiO_2 to water [23–25] and air purification [26–33] because TiO_2 has not only an excellent photocatalytic activity but is also highly chemically stable, non-toxic and inexpensive. However, since the concentration of pollutants in air is quite low, the efficiency of the photocatalytic activity is very low due to its small specific surface area and low adsorption ability.

Clays have been used in combination with TiO_2 photocatalyst to enhance the removal of organic pollutants. Clay-TiO_2 composites have been studied as photocatalytic materials with good absorption ability [34–44]. Ménesi et al. [41] reported that VOCs are degraded at a significantly higher efficiency on TiO_2/Ca-montmorillonite composites than on pure TiO_2. Kameshima et al. [43] reported that the photocatalytic decomposition of 1,4-dioxane by TiO_2/montmorillonite composites was more efficient than for pure anatase (TiO_2) due to the synergy effect of adsorption for 1,4-dioxane and photodecomposed intermediates by montmorillonite and its photodecomposition by TiO_2. Kibanova et al. [44]

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also reported that synthetic hectorite-TiO_2 composites favored the adsorption and enhanced the photocatalytic degradation of VOCs. The photocatalytic activity of kaolinite-TiO_2 composites formed by deposition of TiO_2 on the external surface of kaolinite, was also enhanced. Thus, clay-supported TiO_2 photocatalysts can potentially improve the performance of air treatment techniques because of enhanced adsorption and reactivity of the target VOCs.

Imogolite is an aluminosilicate with a single-walled nanotubular structure consisting of a layer of aluminum(III) hydroxide (gibbsite), with isolated silicate groups bound on the inner wall [45]. The synthesis and properties of imogolite have been investigated over many years [45–48], and imogolite nanotubes have also been investigated for use as a catalyst support [49], methane storage [50,51], and as heat exchange materials [52]. Imogolite is expected to be a superior absorbent due to its large specific surface area arising from its nanotubular structure. However, the removal and photodegradation of VOCs using imogolite-TiO_2 composites has not been investigated.

The present is focused on imogolite which exhibits high photocatalytic activity under visible light irradiation [53], and Cu(II)-grafted TiO_2, which is an absorbent and visible-light-driven photocatalyst [54]. The imogolite was synthesized by a hydrothermal method, and the removal and photodegradation activity of acetaldehyde gas by imogolite and TiO_2 or Cu(II)-grafted TiO_2 composites was evaluated at various relative humidity condition under UV and fluorescent light irradiation.

2. Experimental

2.1. Materials

Tetrasodium silicate *n*-hydrate ($2Na_2O\,SiO_2 \cdot nH_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, 99.9%), nitric acid (HNO_3, 65%), ammonia solution (NH_4OH, 28%), copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, 99.9%), titanium(IV) oxide powder (rutile form, TiO_2, grain size 5 μm, 99.9%) were purchased from Wako Pure Chemical Industries, Tokyo, Japan. Water was purified by using a Millipore installation.

2.2. Synthesis of Imogolite

Imogolite powder samples were synthesized by the hydrothermal method shown in Fig. 1. Tetrasodium silicate *n*-hydrate solution (0.10 mol/L) and aluminum nitrate nonahydrate solution (0.25 mol/L) were mixed in a Si/Al = 0.4 molar ratio. After stirring for 90 min, 28% ammonia solution was slowly added and the solution stirred vigorously to adjust the pH to around 6 and form a gel-like precursor which was dispersed in distilled water and separated by centrifugation at 5000 rpm for 15 minutes. The washing and centrifugation was repeated at least 3 times to remove unreacted ions. The centrifuged product, in which the Si is assumed to be 12.5 mmol/L, was suspended in distilled water, nitric acid solution (1.0 mol/L) was added and stirred to adjust the pH to approximately 4. The suspension was sealed in a Teflon-lined stainless steel autoclave (50 mL) and heated at 100 °C for 48 h to give a transparent suspension from which the imogolite was precipitated by adding 28% ammonia solution. Finally, the precipitated samples were separated by centrifuging (6000 rpm for 30 min), washed with distilled water several times and dried at 80 °C for 1 day.

2.3. Preparation of Cu(II)-Grafted TiO_2

The Cu(II)-grafted TiO_2 photocatalyst was prepared by the impregnation method as previously described [53], using $CuCl_2 \cdot 2H_2O$ as the source of Cu(II). TiO_2 powder (1.0 g; 1.25×10^{-2} mol) was dispersed in 10 mL of distilled water. $CuCl_2 \cdot 2H_2O$ was weighed so that the weight fraction of Cu relative to TiO_2 was 1.0×10^{-3} (i.e., molar ratio of $Cu/TiO_2 = 0.13$). The $CuCl_2 \cdot 2H_2O$ was then added to the aqueous TiO_2 suspension and heated at 90 °C for 1 h with stirring in a vial reactor. The powder samples were separated from the suspension by centrifuging (6000 rpm for 30 min), washed with distilled water, dried at 110 °C for 24 h and finely ground using an agate mortar.

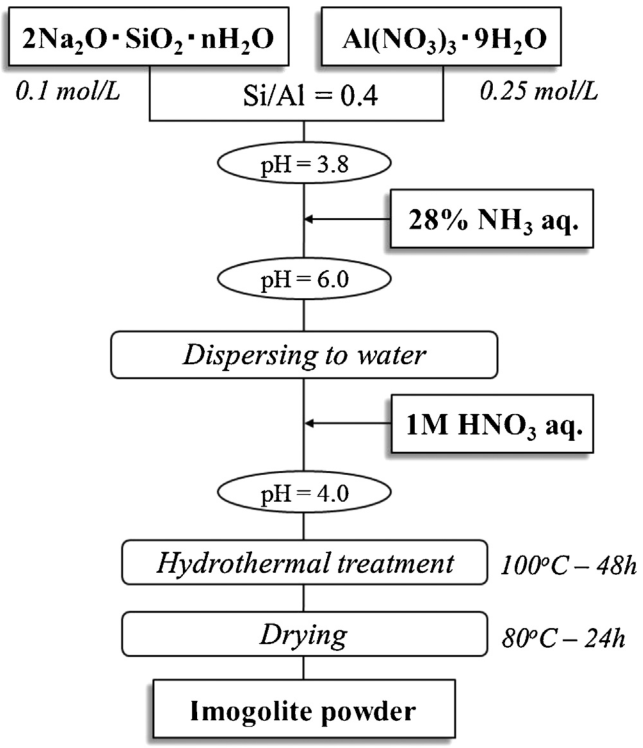

Fig. 1. Synthesis flowchart of imogolite powder by the hydrothermal method.

2.4. Preparation of Imogolite and TiO_2 or Cu(II)-Grafted TiO_2 Composites

The synthesized imogolite powders were dried at 80 °C for 2 days in a vacuum oven to remove the surface adsorbed water. The imogolite powder and TiO_2 or Cu(II)-grafted TiO_2 photocatalyst were then mixed using an agate mortar. The mixed mass ratios were as follows; TiO_2:imogolite = 1:0, 1:0.5, 1:1, 1:2, 1:3, 1:4, and Cu(II)-grafted TiO_2: imogolite = 1: 0, 1: 3. The samples with different mixed mass ratio are denoted in this report as "**TiO_2 X-imo**" and "**Cu-TiO_2 X-imo**" (X indicates mixed mass ratio of imogolite).

2.5. Characterization

The crystalline phase in the samples was identified using a powder X-ray diffractometer (XRD, RINT2100; Rigaku, Japan) with monochromated Cu Kα radiation. The applied voltage and current to the Cu target was 40 kV-40 mA. IR spectroscopy was performed using a Fourier transform infrared spectrometer (FT-IR, JIR-7000; JEOL, Japan). The surface microstructures of the samples were examined by field emission-scanning electron microscopy (FE-SEM, S-4800; Hitachi, Japan) using an acceleration voltage of 5 kV. The morphology of the samples was investigated using TEM (HF-2000; Hitachi, Japan) operating at 200 kV. The samples for TEM were prepared by dispersing one drop of the sample in water and depositing on an amorphous carbon grid. To characterize the local structure around the Si^{4+} and Al^{3+} in the samples, theis ^{29}Si and ^{27}Al solid state MASNMR spectra were acquired using a solid-state NMR