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Rapid and complete oxidation of acetaldehyde on TiO_2 photocatalytic filter supported by photo-induced activated hydroxyapatite

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Abstract

The new TiO_2 photocatalytic filter supported by photo-induced activated hydroxyapatite (HAp $Ca_{10}(PO_4)_6(OH)_2$) was developed and the complete oxidation of acetaldehyde on the filter was investigated. The photocatalytic filter was fabricated by coating TiO_2 and HAp on the porous ceramics body. In the decomposition of acetaldehyde using this composite filter, CO_2 generation came to maximum at 20 min after starting of UV (254 nm) irradiation and the value was the stoichiometric to the complete oxidation. The rapid and complete oxidative decomposition of acetaldehyde can be achieved using the new photocatalytic composite filter in spite of the very small contact time, about 0.4 s through the filter and one path method. This effect would not be explained alone by the absorption capacity of HAp for acetaldehyde. Synergic and composite effect of HAp followed by radical formation under light is maximum at 254 nm.

Keywords: Hydroxyapatite; Titanium dioxide; Photo-induced excitation; Photocatalytic filter; Photocatalytic decomposition; Acetaldehyde

1. Introduction

Hydroxyapatite is known to be a useful and practical biomaterial and an absorbent for chromatography. It also exhibits thermal catalytic activities in many reactions, e.g. dehydrogenation and dehydration of alcohol [1,2], the synthesis of phenol [3,4]. Since hydroxyapatite is very safe for human life, it is an extremely promising candidate for the environmental protection materials. For example, the volatile chlorinated organic compounds such as trichloroethylene and tetrachloroethylene were oxidatively decomposed over calcium-deficient hydroxyapatite at 450–500 °C [5–7]. In this process, the catalytic behavior largely depended on the crystalline structure as described by Vedrine [8].

Recently, it has been recognized that 'atomic transfer' induced by electron- or photo-excitation takes place on a variety of inorganic materials. This provides an effective methodology in the development of 'new materials science by electronic excitation'. Kanai and Matsumura reported the generation of oxygen radical on stoichiometric hydroxyapatite (HAp) under UV irradiation [9].

The author et al. showed that the oxidative decomposition of odor compounds such as methyl mercaptane (MM) and dimethyl sulfide (DMS) occurred effectively on HAp under UV (254 nm) irradiation [10–12]. The XPS, FT-IR and ESR characterizations revealed that UV irradiation modified the PO_4 groups on the HAp surface, and generated a trapped electron and active $O_2^{\bullet -}$ species. The oxygen was thought to be activated due to the electron trapped on the vacancy in the HAp, followed by formation of the labile $O_2^{\bullet -}$ species.

On the other hand, the anatase type TiO_2 is a typical photocatalyst. Though there are some reports on TiO_2/HAp composite filter [13,14], the filter samples reported were those that HAp was formed on TiO_2 photocatalytic filter by soaking treatment and the role of HAp was absorbent material for acetaldehyde or methylene blue. In our study, an active HAp under photo-induced excitation was coated on alumina substrate with three-dimensional framework structure as an adhesive and then TiO_2 was dip-coated to the composite ma-

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terial. This new-type composite filter is expected to have a co-photocatalytic effect of TiO_2 and HAp under UV irradiation. Furthermore, there are few reports on the rapid and complete oxidation of acetaldehyde on photocatalyst, though the many studies on the photocatalytic decomposition of acetaldehyde were reported [15–18].

In this study, the photo-induced active HAp was added to a TiO_2 photocatalytic filter to make a breakthrough in the decomposition of acetaldehyde. The complete oxidative decomposition of acetaldehyde was investigated on the new composite photocatalytic filter.

2. Experimental

The new TiO_2/HAp composite filter was prepared as follows; HAp (Spherial type, Taihei Chemical Industrial Co.) was coated on alumina substrate with three-dimensional framework structure as an adhesive and then anatase type TiO_2 (P25, Degussa) was dip-coated to the composite material. The resulting composite material was dried at 110 °C for 1 h.

The powder samples of alumina, TiO_2/alumina and TiO_2 /HAp/alumina composite filters were characterized. Specific surface areas of these samples were measured with a Mountec Macsorb HM Model-1210 surface area meter. X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT1500 diffractometer using Cu Kα radiation. The surface phases were identified by scanning electron microscopy (SEM; Hitachi S-3200N) with energy dispersion X-ray analysis (EDX). UV–vis reflection spectra were measured with a Shimadzu UV-3100PC spectrometer equipped with an integrating sphere MPC-3100.

The activity of the new photocatalytic TiO_2/HAp composite filter was estimated using a reaction vessel shown in Fig. 1. Photocatalytic reaction of acetaldehyde, a typical air pollutant, was performed at 1 L min^{-1}. The light source used was UV (254 nm)-type (Toshiba Lightec Co., 20W × 2) and UV (365 nm)-type (National Co., 20W × 2). The reaction vessel was covered with aluminum foil to shut out the outside light. Acetaldehyde in inlet and effluent gas was sampled with the syringe (1 mL) and determined by gas chromatograph (Shimadzu GC-17A) with a flame ionization detector. The decomposition of acetaldehyde was also estimated by CO_2 generation. CO_2 in the outlet of the vessel was determined by CO_2 analyzer (Thermo Electron, Model41C-HL). The size of the filter used was 50 mm × 50 mm × 12 mm.

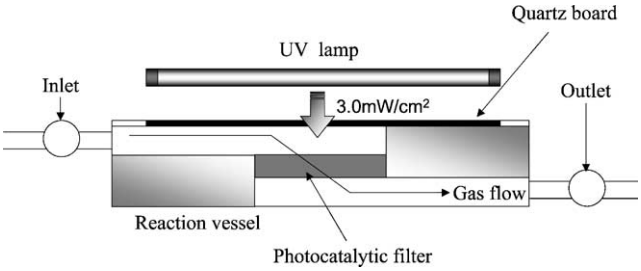

Fig. 1. Reaction vessel to evaluate the activity of photocatalytic filter.

3. Results and discussion

3.1. Characterization of composite filters

The outward appearance of TiO_2/HAp/alumina composite filter is shown in Fig. 2. The specific surface areas of the powdered alumina, TiO_2/alumina and TiO_2/ HAp/alumina filters were 0.24, 0.90 and 0.48 m^2/g, respectively. Though the surface areas of these samples are not large, the sample gas seems to make effectively contact with photo-catalyst, which is TiO_2 or HAp, by the three-dimensional framework structure.

XRD patterns of the samples were shown in Fig. 3. Alumina filter (No. 1) contains corundum type alumina (α-Al_2O_3) and a small amounts of SiO_2, which is impurities in the filter material. In addition, the anatase type TiO_2 appeared in TiO_2/alumina filter (No. 2). The patterns of HAp were not detected in TiO_2/HAp/alumina composite filter (No. 3) because of a low number of small particles to small in size to be detected. The EDX spectra of No. 3 filter were measured as shown in Fig. 4. The peaks of Ca and P appeared in addition to Al, Ti, Si and O in the spectra. The result shows that No. 3 filter contains HAp on the surface of the material.

UV–vis reflectance spectra of these samples were shown in Fig. 5. The absorbance of TiO_2/alumina filter (No. 2) in the range 210–380 nm increased with TiO_2 coating. Though the absorbance of TiO_2/HAp/alumina composite filter (No. 3) slightly decreased than that of TiO_2/alumina filter (No. 2) in the same range, the photocatalytic activity of the filter seemed to be scarcely influenced, especially under 320 nm.

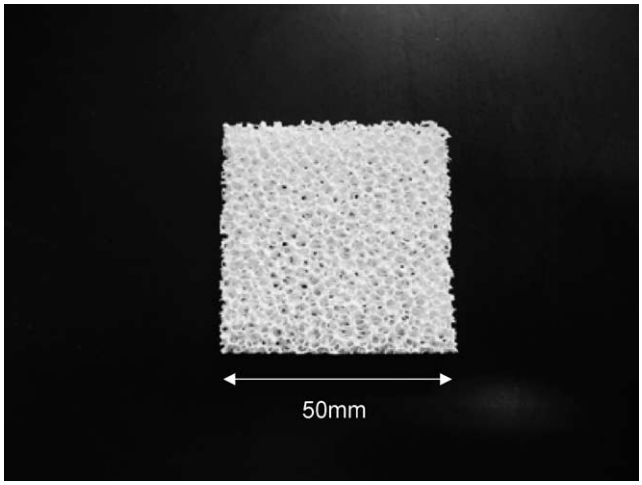

Fig. 2. Outward appearance of TiO_2/HAp/alumina filter.

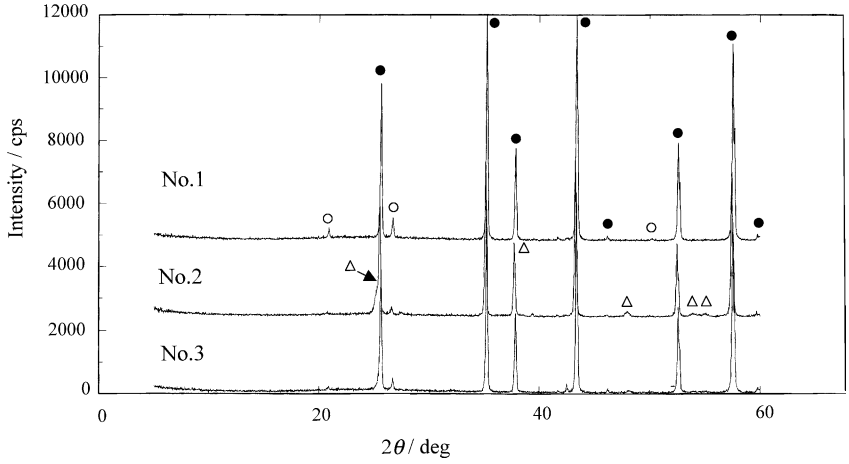

Fig. 3. XRD patterns of the filter samples. No. 1: alumina filter; No. 2: TiO_2/alumina filter; No. 3: TiO_2/HAp/alumina filter (●) α-Al_2O_3, (◯) SiO_2, (△) TiO_2 (anatase).

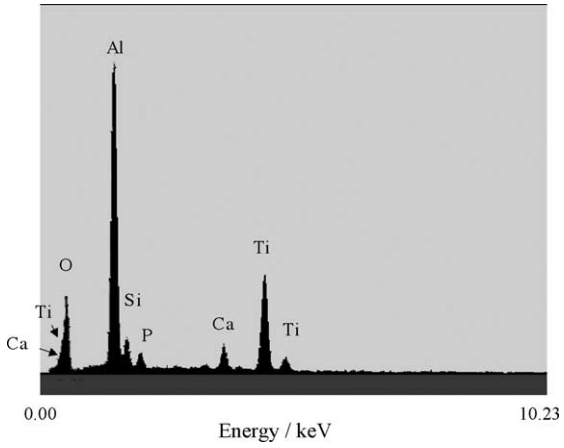

Fig. 4. EDX spectra of No. 3 filter.

3.2. Photocatalytic decomposition of acetaldehyde on TiO_2/HAp/alumina composite filter

The generation of CO_2 in the decomposition of acetaldehyde (13.0 ppm) on the TiO_2/HAp/alumina photocatalytic filter was investigated under UV (365 nm) and UV (254 nm) irradiation in the reaction system shown in Fig. 1. The composite filter (TiO_2/HAp (20 wt% to TiO_2 amount)/alumina) was examined and the results are shown in Fig. 6. Under irradiation of UV (365 nm), CO_2 generation was less than 81% of the theoretical generation value, 26.0 ppm, to the complete oxidation of acetaldehyde. On the other hand, CO_2 generation was about 96% of the stoichiometric amount under irradiation of UV (254 nm) on the filter. In the previous papers [10,12], it was shown that MM and DMS decomposed on HAp under UV (254 nm) irradiation. However, acetaldehyde hardly decomposed on HAp/alumina filter even under UV (254 nm) irradiation, and the decomposition of acetaldehyde was not complete on TiO_2/alumina photocatalytic filter under the same condition. These results would indicate that the co-photocatalytic effect with TiO_2 and HAp appears under UV (254 nm) irradiation for the acetaldehyde decomposition. The oxidative decomposition of acetaldehyde proceeded very effectively using the new TiO_2/HAp/alumina photocatalytic filter and UV (254 nm) irradiation.

Furthermore, CO_2 generations in the decomposition of acetaldehyde using various types of composite filters were com-

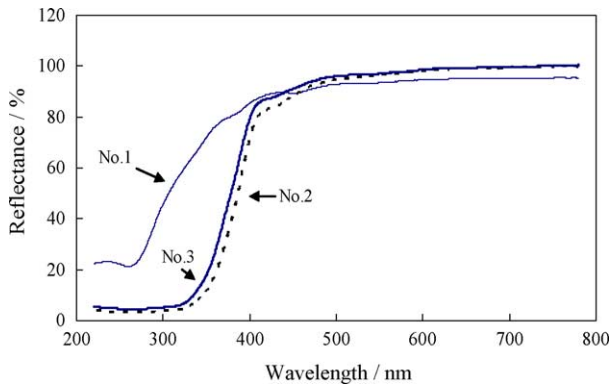

Fig. 5. UV–vis reflectance spectra of the filter samples. No. 1: alumina filter; No. 2: TiO_2/alumina filter; No. 3: TiO_2/HAp/alumina filter.

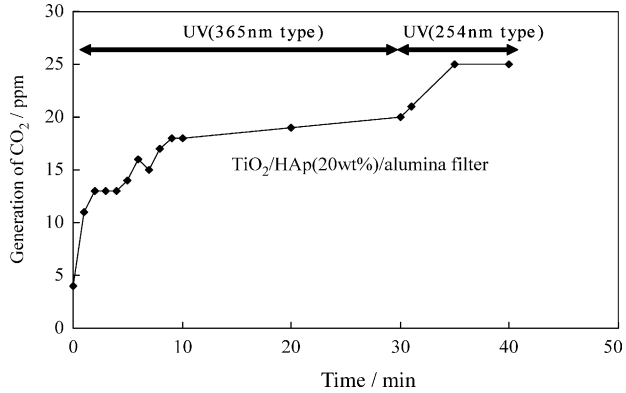

Fig. 6. Generation of CO_2 in the decomposition of actealdehyde on the photocatalytic filter. Acetaldehyde: 13 ppm; flow-rate: 1 L min^{-1}.

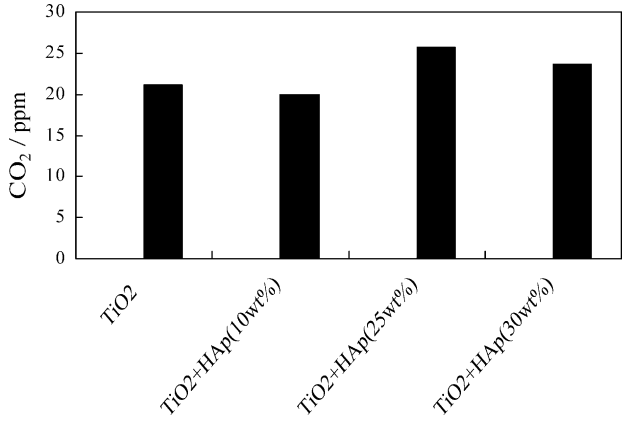

Fig. 7. Comparison of CO_2 generation in the decomposition of acetaldehyde on each photocatalytic filter under UV (254nm type) irradiation. Acetaldehyde: 13 ppm; flow-rate: 1 L min^{-1}.

pared under UV (254 nm) irradiation. The results are shown in Fig. 7. The average generation of CO_2 in 10–30 min after starting irradiation using TiO_2/HAp (25 wt.%)/alumina filter was the higher than that using the other components, and the CO_2 generation was almost equal to the stoichiometric amount to the complete oxidation of acetaldehyde, though the CO_2 generation stayed to be 81% using TiO_2/alumina photocatalytic filter.

After 20 min irradiation, the CO_2 generation in the decomposition of acetaldehyde on TiO_2/HAp (25 wt.%)/alumina filter reached the maximum, that is the stoichiometric value to the complete oxidation, and then the complete oxidative decomposition continued. Generally, the activation time of TiO_2 is less than 5 min after starting UV irradiation. On the other hand, HAp needs the activation time over 10 min under UV irradiation as mentioned in previous paper [10]. These facts indicate that the HAp activation followed by radical formation by UV (254 nm) irradiation contributes to the complete oxidation of acetaldehyde to CO_2 on the TiO_2/HAp/alumina composite filter. This effect would not be explained alone by the absorption capacity of HAp for acetaldehyde. The adsorbed acetaldehyde on HAp is degraded very efficiently by the TiO_2 under light reflecting a good contact between the TiO_2 and HAp. Furthermore, acetaldehyde can be oxidated completely to CO_2 on the new composite filter in spite of the very small contact time, about 0.4 s through the filter and one path method.

4. Conclusion

The very rapid and complete photocatalytic decomposition of acetaldehyde could be achieved using the new TiO_2/HAp/alumina composite filter. That is, CO_2 generation came to the stoichiometric value to the acetaldehyde decomposition on the new composite filter under UV (254 nm) irradiation. These findings would indicate that co-photocatalytic effect of TiO_2 and HAp appears on the filter under the condition.

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