Photodeposition of manganese oxide on titanium dioxide fixed filter and its application to environmental purification

(二酸化チタン固定化フィルターによるマンガン酸化物の光析出及び環境浄化への応用)

4ASCM001 Takanobu OHASHI
Supervisor Dr. Yoshika SEKINE

Introduction

Photocatalytic deposition of metal ions onto semiconductor powders has been received considerable attention in relation to a preparation of metal loaded semiconductor catalyst, application to treatment of water polluted by heavy metals and so on. Previous studies have reported Ag^+, Au^{3+}, Cu^{2+}, Pt^+ and Pd^{2+} could be photodeposited onto titanium dioxide (TiO_2) under irradiation of ultraviolet rays[1). As for manganese, authors have successfully prepared manganese-titanium complex oxide by photodeposition method using $KMnO_4$ as a starting substance and TiO_2 powder[2). The complex oxide showed significant removal efficiency for harmful formaldehyde (HCHO) gas and released carbon dioxide as a major product. However, the powder-like material has a difficulty in handling and is not suitable for practical uses. In this study, photocatalytic deposition of manganese oxide was carried out on the surface of the flat glass fiber filter on which TiO_2 had been fixed by sintering impregnated titanium tetraisopropoxide (TTIP). And then, the filter-like complex oxide was tested to remove the formaldehyde gas with and without UV irradiation.

Experimental

Preparation of titanium dioxide fixed filter : Glass fiber filter (Whatman, GF/B Circles, 47mmφ) was dipped into 70% TTIP/2-propanol and dried in air. Then it was calcinated for 3 hours from 100 to 700℃ by an electric furnace. Eight types of filters were prepared including the one without calcination.

Photodeposition of manganese oxide : Photodeposition method of manganese oxide was illustrated in Fig.1. Titanium dioxide fixed filter was added to 100mL of 1.4×10^{-4}M $KMnO_4$ aqueous solution in a glass beaker. It was then irradiated by UV (100μW/cm^2) from top of the beaker in an irradiation reactor. Aqueous Mn concentration was determined by Polarized Zeeman Atomic Absorption Spectrophotometer (Z-5300, Hitachi).

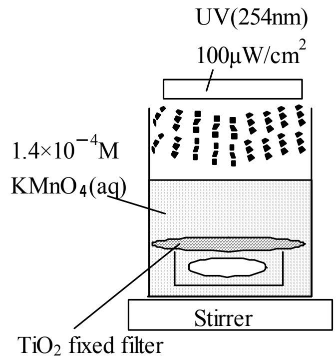


Fig.1 Photodeposition of manganese oxide on TiO_2 fixed filter

Examination of photodeposition condition : Since photodeposition rate of manganese oxide depends on utilization efficiency of electron in conduction band and redox potential which varies with pH, such effects were examined by addition of organic compounds as reductant and control of pH of the solution by adding HNO_3(aq).

Characterization of the filter surface : The prepared filter, titanium dioxide fixed filter and manganese-titanium complex fixed filter, were observed by a scanning electron microscopy (JSM-6301F, JEOL). Crystalline type of the titanium dioxide and manganese-titanium complex on the filter was identified by a XRD(RigakuDenki,Gaigerflex RAD-C).

Removal of formaldehyde by the complex oxide : Schematic view of the mass balance study was shown in Fig.2. Under atmospheric pressure at room temperature, the prepared manganese-titanium complex fixed filter was placed in a 20L of sampling bag made of polytetrafluoroethylene. Dry air (Pure air, G2 grade, CO_2 free, Nippon Sanso) was passed through the surface of the formaldehyde aqueous solution (7.4%), and HCHO gas (150mg/m^3) was introduced in the reaction bag. And then, the bag was closed with and without UV irradiation by a black light. HCHO was collected in 0.5%-boric acid aqueous solution and spectrophotometrically determined by AHMT method. Concentration of CO_2 was measured by gas chromatography (Shimadzu GC-8A).

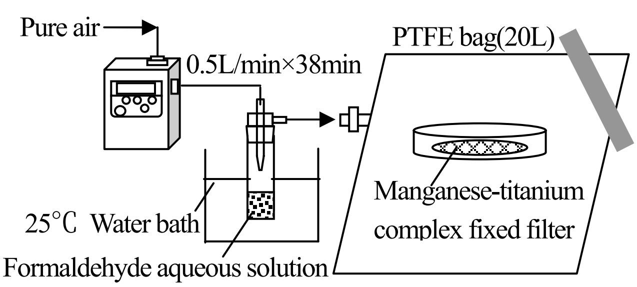


Fig.2 Schematic view of the mass balance study

Results and experimental system discussion

Using $KMnO_4$ as a starting substance, concentration of Mn in the aqueous solution gradually decreased under UV irradiation. At the same time, color of the surface of TiO_2 fixed filter became brown. This suggested photodeposition of manganese oxide was successfully occurred onto the semiconductor surface. In order to maximize the photodeposition rate, we have investigated effects of preparation conditions of the TiO_2 fixed filter on the photodeposition of manganese oxide. The optimum calcination temperature was found 500 degrees. Fig.3 shows overview and SEM image of the TiO_2 fixed filter, after photodeposition of manganese oxide. We confirmed that photodeposited manganese oxide was dispersed on the surface of TiO_2.

Fig.4 shows effect of addition of organic compounds on the photodeposition rate of manganese oxide. While alcohols worked as a good reductant which prevents recombination of hole and electron and hence enhanced the photodeposition rate, 2-butanone, which directly reacts with permanganate, did not work well. On the other hand, the photodeposition rate was also enhanced by increasing pH. This is probably because adsorption of permanganate was encouraged in the acidic solution where the surface of TiO_2 became positive.

Using this manganese-titanium complex fixed filter, removal of HCHO was investigated. Fig.5 shows results of time-courses of concentrations of HCHO and CO_2 in the reaction bag. In a dark reaction, the prepared Manganese-titanium complex fixed filter showed removal efficiency of HCHO and yield of CO_2 by function of manganese oxides. Comparing dark reaction, UV irradiation on the Manganese-titanium complex fixed filter enhanced the removal efficiency and production of CO_2. This means synergic effect of manganese and titanium oxides on the removal of harmful HCHO in air.

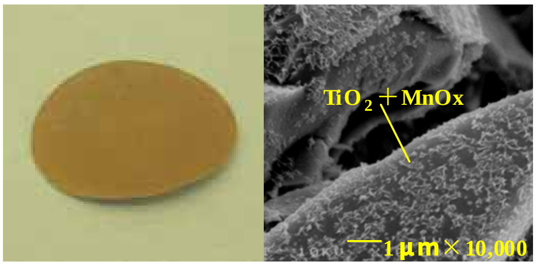


Fig.3 Overview (left) and SEM image (right) of the TiO_2 fixed filter, after photodeposition of manganese

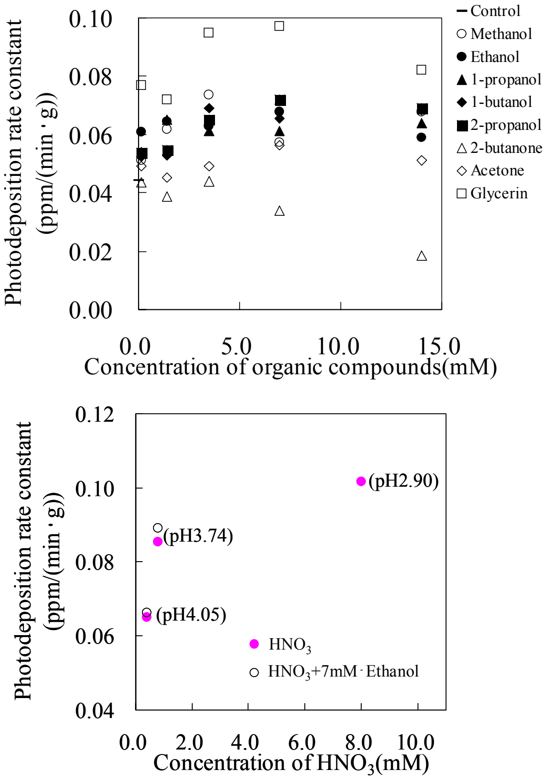
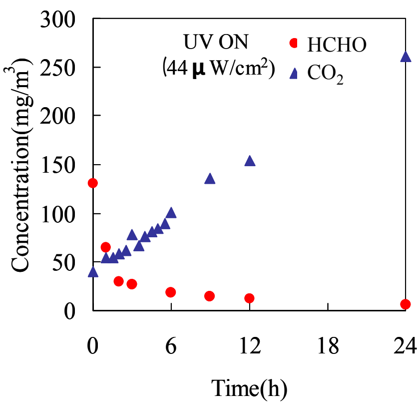


Fig.4 Effect of additives on the photodeposition



1.10mgMn/gTiO_2

Fig.5 Time-courses of concentrations of HCHO and CO_2

Conclusion

Manganese-titanium complex filter was successfully prepared by the photodeposition method using $KMnO_4$ and TiO_2 fixed filter. Photodeposition rate of manganese oxide was increased most by controlling pH of the solution. The complex filter decomposed formaldehyde into carbon dioxide at room temperature. And UV irradiation enhanced the production of the carbon dioxide. Therefore, it was confirmed that synthesized catalyst showed synergic effect of manganese oxide and titanium dioxide on the removal of harmful formaldehyde in air.

Reference

1) Otani, B., *Kagaku Kogyo*, 1988(3), 219-226(1988)

2) Tateoka, A., Sekine, Y., Tsuda, T., Ohashi, T., *Mat. Sci., Forum*, 480-481, 117-122(2005)