

Study on Photocatalytic Deposition of Manganese Oxide

onto Nano-order Titania Particles

(酸化チタンナノ粒子へのマンガン酸化物の光析出)

2ASCM014 Ayumu TATEOKA
 Supervisor Mikio WATANABE
 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 and application to treatment of water polluted by heavy metals. Previous studies reported Ag^+ , Au^{3+} , Cu^{2+} , Pt^+ and Pd^{2+} could be photodeposited onto titanium dioxide (TiO_2) under irradiation of ultraviolet rays. As for manganese, author can not find a report on the photodeposition Mn^{2+} using TiO_2 . Manganese dioxide (MnO_2) is extensively used in various catalytic processes of environmental purification, including oxidative decomposition of formaldehyde (HCHO)¹, carbon monoxide, ozone and odor gases. In this study, photodeposition of manganese oxide onto the TiO_2 surface was developed and a mass balance examination was conducted for the products through the reaction between HCHO and the prepared Mn-Ti complex oxide.

Experimental

Photodeposition of manganese oxide. The titanium dioxide was used anatase type powder (ST-01, Ishihara Sangyo) whose particle diameter was 7nm with $315\text{m}^2/\text{g}$ of BET surface area. To 100mL of $1.4 \times 10^{-4}\text{mol/l}$ KMnO_4 and $1.4 \times 10^{-4}\text{mol/l}$ MnCl_2 solutions, 0.3g of TiO_2 was added and suspended in a glass beaker. Each suspended solution was then irradiated from top and bottom of the beaker in irradiation reactor ($130\mu\text{W}/\text{cm}^2$). During the reaction, aliquot of the suspension was sampled and filtered (Millex-LG, Millipore, $<0.20\mu\text{m}$). Concentration of manganese ions in the time-series supernatant were determined by Polarized Zeeman Atomic Absorption Spectrophotometer (Z-5300, Hitachi).

Observation of Mn-Ti complex oxide. To 300ml of $4.64 \times 10^{-3}\text{mol/l}$ potassium permanganate solution, 1.2g of TiO_2 was added and suspended. After UV irradiation as described above for a week, completed complex oxide was filtered and vacuum dried. The prepared powders were then observed by a scanning electron microscopy (JSM-6301F, JEOL).

Removal of formaldehyde by the complex oxide. Schematic view of the experimental system was shown in Fig.1. Under atmospheric pressure, the prepared Mn-Ti complex oxide (0.3g) was dispersed on a petri dish and placed in a 20L of sampling bag made of polytetrafluoroethylene at room temperature. Dry air (Pure air, G2 grade, CO_2 free, Nippon Sanso) was passed through the surface of the formaldehyde solution (10%), and HCHO gas ($200\text{mg}/\text{m}^3$) was introduced in the reaction bag. And then, the bag was closed with and without UV irradiation by a black light. After 24hours, concentrations of HCHO

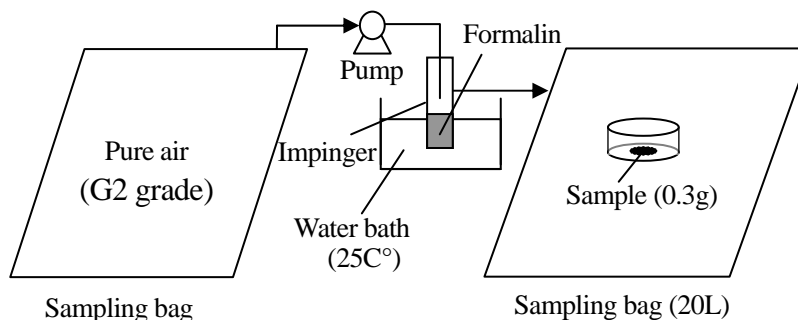


Fig.1 Schematic view of the for the evaluation of HCHO removal efficiency.

and CO_2 in the bag were measured and compared with initial ones. HCHO was collected in 0.5%-boric acid solution and spectrophotometrically determined by AHMT method. CO_2 was measured by gas chromatography (Shimadzu GC-8A). And formate ion was extracted from used complex oxide by 10ml of 100mM Na_2CO_3 with mild shaking and determined by ion chromatography (ICS-90, Dionex).

Results and experimental system discussion

Fig.2 shows time courses of supernatant concentrations of Mn ion during the photoredox reaction of TiO₂ using KMnO₄ and MnCl₂. Using KMnO₄ as a starting substance, concentration of Mn in the aqueous solution gradually decreased after UV irradiation. At the same time, color of the surface of TiO₂ became brown. This suggested photodeposition of Mn⁷⁺ onto the semiconductor surface. In contrast, the concentration in MnCl₂ solution was dropped initially, but became constant even when UV light on. The color of the semiconductor did not change. The initial drop may be caused by adsorption of Mn ion on the TiO₂ surface. As a result, it was reconfirmed that TiO₂ did not photodeposit Mn²⁺ onto the surface.

Fig. 3 shows a SEM image of the product. The diameter of the particle was found to be about 80 nm. Considering diameter of TiO₂ particle (7nm), complex oxide might congregate in the present image.

Using this complex oxide, removal of HCHO was investigated. Table 1 shows results of mass balance study on the reaction between HCHO and the catalyst. In a dark reaction, the prepared Mn-Ti oxide showed higher removal efficiency, *R* of HCHO and yield of CO₂ comparing with those by TiO₂. Adsorbed HCHO may be accounted as unknown at Run 1. Comparing Run 2 and 3, UV irradiation on the Mn-Ti complex enhanced the removal efficiency and production of CO₂. This means synergic effect of manganese and titanium oxides on the removal of harmful HCHO in air. However, further investigation on the reaction mechanism was need, because the formate, which might cause poisoning of MnO₂, was still found on the surface of the complex in some extent under UV light.

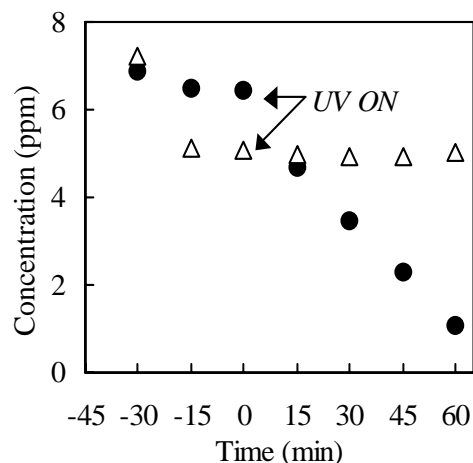


Fig.2 Supernatant Mn concentration versus irradiation time for suspended solutions.

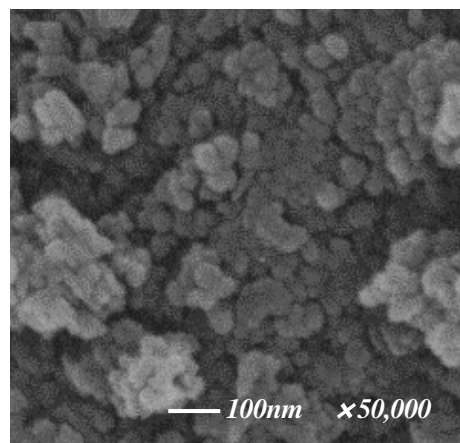


Fig.3 SEM image of manganese-titanium complex oxide.

Table 1 Mass balance table of the HCHO removal experiments (Amount of substances found in the sampling bag are shown in mmol. Numbers in parenthesis show yields in %).

Run	Type	UV	Initial	after 24hrs			R(%)
			HCHO	HCHO	CO ₂	HCOO ⁻	
1	TiO ₂ (ST-01)	off	0.120	0.043	0.016 (21)	0.005 (6.5)	64
2	Mn-Ti oxide	off	0.160	0.028	0.036 (27)	0.110 (83)	83
3	Mn-Ti oxide	on	0.150	0.018	0.043 (33)	0.110 (83)	88

Conclusion

Nano-order particles of manganese-titanium complex oxide were successfully prepared by the photodeposition method using KMnO₄ as a starting substance and TiO₂. The complex oxide decomposed formaldehyde into carbon dioxide at room temperature. And UV irradiation enhanced the production of the carbon dioxide. Therefore, it was confirmed that the synthesized catalyst showed synergic effect of manganese dioxide and titanium dioxide on the removal of harmful formaldehyde in air.

Reference

- 1) Y. Sekine, *Atmospheric Environment*, **36**, 5543-5547, (2002).