Adsorption and photocatalytic decomposition of odor compounds containing sulfur using TiO_2/SiO_2 bead

Harumitsu Nishikawa [a,*], Yasumitsu Takahara [b]

[a] *Gifu Prefectural Institute of Health and Environmental Sciences, 1-1, Naka-Fudogaoka, Kagamigahara-shi, Gifu 504-0838, Japan*
[b] *Gifu Prefectural Livestock Research Institute, 3-8, Maehira-cho, Minokamo-shi, Gifu 505-0037, Japan*

Abstract

Adsorption and photocatalytic decomposition of dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) using an improved type of silica bead inner-supported with TiO_2 (TiO_2/SiO_2) were investigated. The specific surface area of the TiO_2/SiO_2 bead was $321\,m^2\,g^{-1}$ and the adsorption capacity of the bead for DMS or DMDS was 49.9, $116\,\mu g\,g^{-1}$, respectively. Photocatalytic decomposition of DMS using the bead was about 100% at the space velocities of 33.5–$134\,h^{-1}$ after the equilibrium between adsorption and desorption of the compound, whereas, that of DMS using surface-supported TiO_2/SiO_2 was below 65% at the same conditions as described in previous paper. Though photocatalytic decomposition of DMDS using the inner-supported bead was below 53% for the same condition as DMS, the removal of DMDS in the lighting up condition from the start using the bead was about 100% for 50 h at a space velocity of $67\,h^{-1}$. It was suggested that DMDS was treated completely by the composite effects of adsorption and photocatalytic decomposition. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalysis; Adsorption; Odor treatment

1. Introduction

Odor compounds containing sulfur, such as methyl mercaptan, dimethyl sulfide (DMS) and dimethyl disulfide (DMDS), are emitted by fermentation treatment of animal feces in livestock industry [1] and from sewage disposal plant, etc. Smells of these compounds are often unpleasant for human life. Odor treatment is important for our comfortable life.

Recently, photocatalyst such as TiO_2 [2–7] has been used for environmental purification, i.e. decomposition of acetaldehyde in air [8,9], oxidation of NO followed by removal as HNO_3 [10], degradation of chlorinated organic compounds in water [11]. However, photocatalytic effect of materials coated with TiO_2 is not adequate in general for rapid treatment of water and air purification.

Uchida et al. reported a method on the use of activated carbon as a supporting material for TiO_2 in photocatalytic degradation of propyzamide [12], a typical herbicide. They recognized that high adsorptive activity of the activated carbon made the compound to concentrate around the loaded TiO_2, resulting in a rapid degradation of the compound. Fukaya et al. proposed a photocatalytic treatment of colored waste water with TiO_2 film coated on silica gel [13]. We also reported on an adsorption effect and photocatalytic decomposition of DMS using SiO_2 bead surface-supported with TiO_2 in a previous paper [14]. The SiO_2 bead is good for flowing of gas, transmission of ultraviolet beam and adsorption of odor compounds.

* Corresponding author.

In this paper, we describe on properties of an improved type of SiO_2 bead inner-supported with TiO_2, comparison of photocatalytic activities between surface- and inner-supported type of the beads and removal efficiencies of DMS and DMDS.

2. Experimental

Two kinds of SiO_2 beads coated with TiO_2 (supplied by Sinto V Cerax Co.) were used as catalysts. One was surface-supported type (TiO_2/SiO_2-A) and another was inner-supported type(TiO_2/SiO_2-B). A commercial TiO_2 grain were examined as a comparison material. The particle size of the materials is 3–4 mm in diameter. Specific surface area and average pore diameter were measured by a Fuji Silisia chemistry nitrogen adsorption meter. Energy dispersive X-ray (EDX) spectra were measured with a Japan Phillips EDAX DX-4. X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT 1500HV diffractometer using Cu Kα radiation.

The experimental apparatus for adsorption and photocatalytic reaction were described in a previous paper [14]. Adsorption test of DMS or DMDS in air was performed at a flow of 100 ml min^{-1}. Photocatalytic reaction of the compounds was performed at the space velocities of 33.5, 67 and 134 h^{-1}. The light source used was a black-light-type lamp (Toshiba Lightec Co., 2 W lamp). Adsorption or photocatalytic reaction vessel was covered with aluminium foil to shut-off the outside light. Sample gas was prepared with pure air (Nippon Sanso Co.). DMS and DMDS in inlet and effluent gas were measured by gas chromatograph (Shimadzu GC-15A) equipped with flame photometric detector. SO_2 in effluent gas was measured by SO_2 analyzer (Japan thermoelectron model 43C). Organic acids collected in water at the outlet of the vessel, or extracted with water from the TiO_2/SiO_2

Table 2
Adsorption capacity of TiO_2/SiO_2-B

Compound	Adsorption capacity (μg g^{-1})	
	TiO_2 grain	TiO_2/SiO_2-B
DMS	1.2	49.9
DMDS	8.4	116

bead after the reaction were measured by ion chromatograph (Shimadzu organic acid analysis system).

3. Results and discussion

3.1. Characterization of two types of TiO_2/SiO_2 beads

Characteristics of the TiO_2/SiO_2 beads and the TiO_2 grain are shown in Table 1. The TiO_2 support ratio of TiO_2/SiO_2-B was about 10 times higher than that of TiO_2/SiO_2-A. Specific surface areas of these beads were 1.5–1.8 times larger than that of the TiO_2 grain.

Fig. 1 shows EDX spectra of TiO_2/SiO_2-B. Titanium was detected both at surface and inner of the SiO_2 bead. On the other hand, titanium in TiO_2/SiO_2-A was detected only at surface of the bead [14]. The crystal form of TiO_2 detected on TiO_2/SiO_2-B was confirmed to be anatase from the measurement of XRD. Tanaka et al. showed that distribution of TiO_2 reached maximum at the 60 μm-depth from the surface of TiO_2/SiO_2-B by the depth analysis of raser-Raman spectroscopy [15]. From these results, TiO_2/SiO_2-B was expected to have the higher photocatalytic activity than TiO_2/SiO_2-A.

3.2. Adsorption of DMS and DMDS

Adsorption capacities of TiO_2/SiO_2-B to DMS and DMDS are shown in Table 2. The adsorption

Table 1
Characteristics of TiO_2 beads and TiO_2 grain

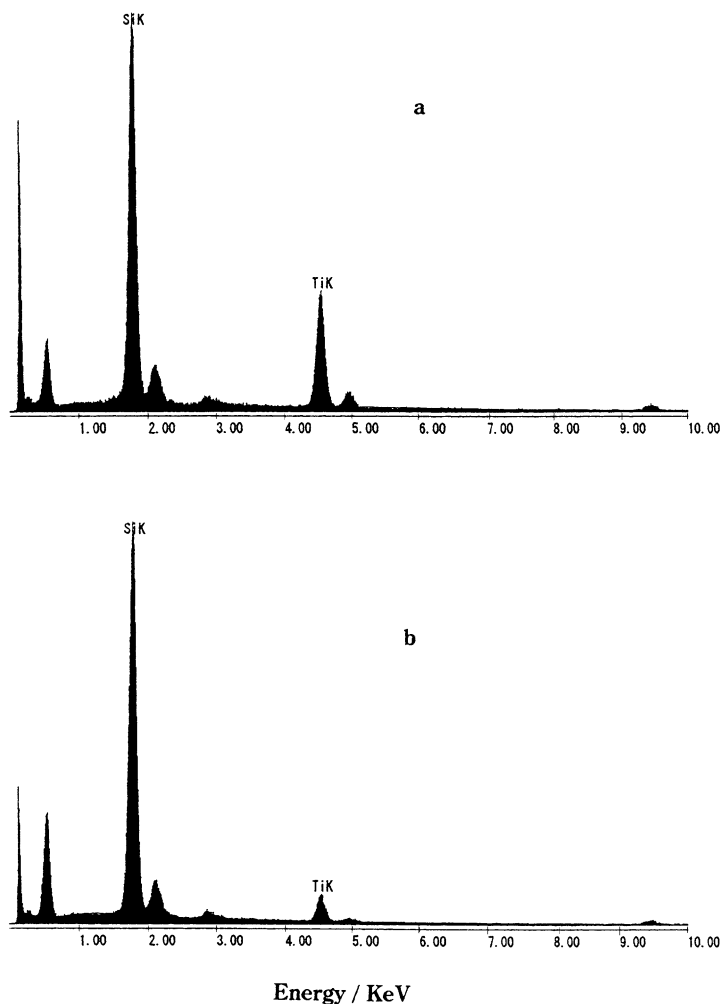| Sample	TiO_2 supported ratio (%)	Surface area (m^2 g^{-1})	Average pore diameter (nm)
TiO_2/SiO_2-A	1.5	391	3.6
TiO_2/SiO_2-B	14	321	13.9
TiO_2 grain	90	214	11.6

Fig. 1. EDX spectra of TiO_2/SiO_2-B: (a) surface; (b) inner.

capacity of TiO_2/SiO_2-B to DMS or DMDS was 42 or 14 times higher than that of the commercial TiO_2 grain, respectively. It is assumed that the adsorption state of the compounds to TiO_2/SiO_2-B is different from that of the TiO_2 grain from the result that the adsorption capacity of the bead to DMS or DMDS was surprisingly high considering the surface area of the bead only about two times than that of the grain. That is, not only physical adsorption, but chemical adsorption due to SiOH at the surface of the bead would participate in the removal of DMS and DMDS. Therefore, TiO_2/SiO_2-B was expected to be suitable for adsorptive treatment of these compounds.

3.3. Photocatalytic decomposition of DMS

The comparison of photocatalytic decomposition efficiencies between TiO_2/SiO_2-A and TiO_2/SiO_2-B after the equilibrium between adsorption and desorption of DMS is shown in Fig. 2. The removals of DMS with TiO_2/SiO_2-B were almost 100% at the space velocities of $33.5–134 \, h^{-1}$, whereas, those with TiO_2/SiO_2-A were below 65% at the same conditions. The results show that the photocatalytic efficiency of TiO_2/SiO_2-B is very superior to TiO_2/SiO_2-A.

The relation between decomposition of DMS with TiO_2/SiO_2-B and production of SO_2 are shown in
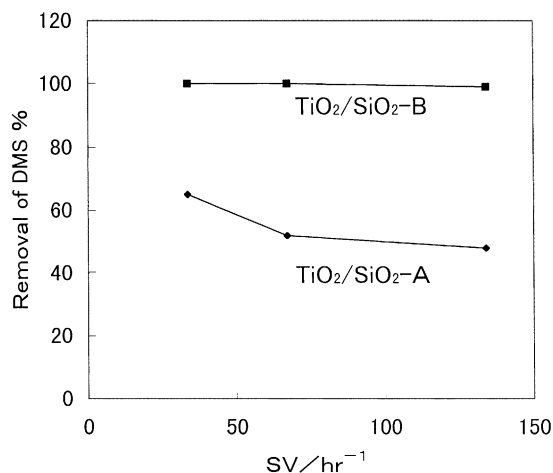
Fig. 2. Photocatalytic decomposition of DMS using TiO_2/SiO_2 beads.

Fig. 3. The concentration of DMS decreased rapidly after lighting up and that of SO_2 became maximum after 15 min from lighting up, decreased slowly and held almost constantly for about 20 min. We have difficulty in the quantitative estimation of SO_2 concentration, because the bead adsorbs also SO_2 fairly well. It is assumed that adsorption effect might be superior to photocatalytic decomposition as a whole and that the decomposition occurred slowly by the diffusion of DMS from the adsorption site to photocatalytic site.
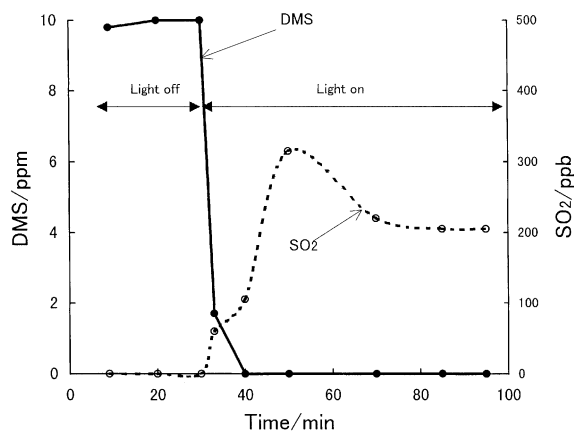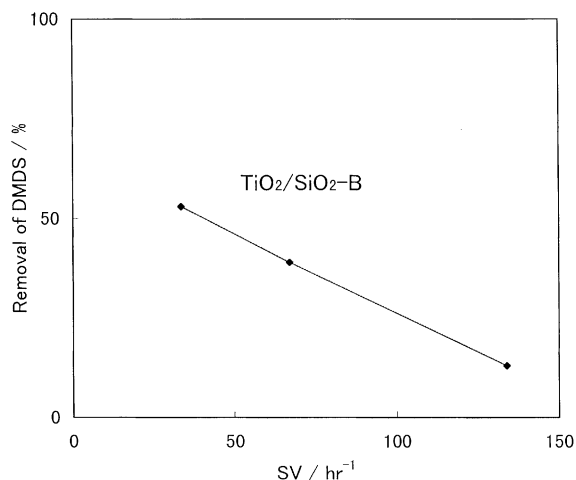

Fig. 3. Decomposition of DMS and production of SO_2.

Fig. 4. Photocatalytic decomposition of DMDS using TiO_2/SiO_2-B.

3.4. Photocatalytic decomposition of DMDS

Photocatalytic decomposition of DMDS using TiO_2/SiO_2-B after the equilibrium between adsorption and desorption of DMDS to the bead is shown in Fig. 4. The removals of DMDS were below 53% at the space velocities of $33.5–134\,h^{-1}$. It was recognized that the decomposition of DMDS was not easy, though DMS decomposed efficiently in the same conditions. So, we examined the time course changes of removal of DMDS using TiO_2/SiO_2-B in the lighting up condition from the start. The removal of DMDS and effluence of SO_2 are shown in Fig. 5. The removals of DMDS were 100% up to 50 h in the
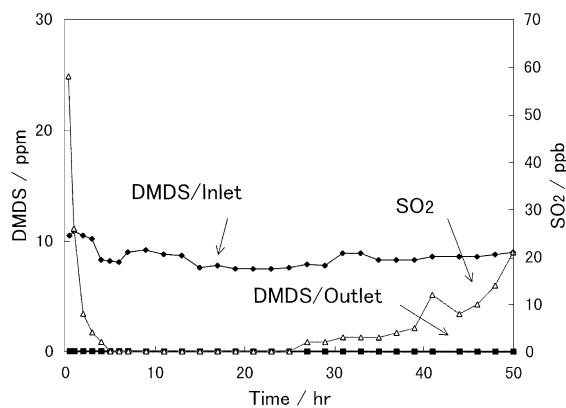

Fig. 5. Removed of DMDS and production of SO_2.

condition, that is, DMDS could be treated completely by both adsorption and photocatalytic decomposition effects. The higher concentration of SO_2 was detected at early stage of the experiment, 5 h after the experiment, it became undetectable in the effluent, and then, was detected again at the last of the experiment. Consequently, it was assumed that adsorption might have occurred preferentially at the SiO_2 site and the photocatalytic decomposition occurred gradually at the TiO_2 site by the diffusion of DMDS molecules. It will be favorable because distribution of TiO_2 maximized in the 60 μm-depth from the surface of TiO_2/SiO_2-B as described above, and the UV-light would be able to reach adequately to the depth.

3.5. Decomposition products of DMS and DMDS

The decomposition product of DMS detected in effluent gas using TiO_2/SiO_2-B catalyst was only SO_2 and the products extracted with water from the bead after the reaction were formic and acetic acid. DMDS determined in the decomposition of DMS using TiO_2/SiO_2-A was not detected in the case of TiO_2/SiO_2-B.

On the other hand, the decomposition products of DMDS detected in effluent gas using TiO_2/SiO_2-B catalyst were SO_2 and formic acid. The products extracted from the bead after the reaction were formic and acetic acid as well as in DMS decomposition. These results show that oxidation of sulfur in DMS or DMDS proceeds very effectively in the photocatalytic reaction with TiO_2/SiO_2-B, which makes marked difference from the decomposition of DMS with TiO_2/SiO_2-A as described in the previous paper [14].

4. Conclusions

1. TiO_2/SiO_2-B, inner-supported catalyst, is effective for adsorptive treatment of DMS and DMDS.
2. The photocatalytic decomposition of DMS with TiO_2/SiO_2-B was almost 100% and that of DMDS was below 53% at the space velocities

of 33.5–134 h^{-1} after the equilibrium between adsorption and desorption of the compounds.
3. It was suggested that the removal of DMS or DMDS from the air using TiO_2/SiO_2-B was performed sufficiently by the combination effect of adsorption and photocatalytic decomposition.
4. Oxidation of sulfur in DMS or DMDS proceeded very effectively in the photocatalytic reaction with TiO_2/SiO_2-B.

Acknowledgements

References

[1] Y. Takahara, K. Kato, R. Inaba, H. Iwata, Jpn. J. Public Health 40 (1993) 29.
[2] T. Inoue, A. Fujishima, K. Konishi, K. Honda, Nature 277 (1979) 637.
[3] I. Izumi, W.W. Dunn, K. Wilbourn, F.F. Fan, A.J. Bard, J. Phys. Chem. 84 (1980) 218.
[4] H.K. Dong, M.A. Anderson, J. Photochem. Photobiol. A: Chem. 94 (1996) 221.
[5] N.N. Lichtin, M. Sadeghi, J. Photochem. Photobiol. A: Chem. 113 (1998) 81.
[6] Z. Hung, P.-C. Maness, D.M. Blake, E.J. Wolfrum, S.L. Smoliski, W.A. Jacoly, J. Photochem. Photobiol. A: Chem. 130 (2000) 163.
[7] B. Pal, M. Sharon, J. Mol. Cat. A: Chem. 160 (2000) 453.
[8] J. Peral, D.F. Ollis, Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993, p. 741.
[9] I. Sopyan, M. Watanabe, S. Murasawa, K. Hashimoto, A. Hujishima, J. Photochem. Photobiol. A: Chem. 98 (1996) 79.
[10] T. Ibusuki, S. Kutsuna, K. Takeuchi, K. shinkai, T. Sasamoto, M. Miyamoto, Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993, p. 375.
[11] M. Murabayashi, K. Okamura, Yosui to Haisui 36 (1994) 877.
[12] H. Uchida, S. Itoh, H. Yoneyama, Chem. Lett. (1993) 1995.
[13] M. Fukaya, H. Taoda, T. Nonami, E. Watanabe, K. Iseda, M. Maekawa, C. Shirai, S. Takeuchi, Z. Yamada, K. Takemura, Y. Nabeshima, in: Proceedings of the 4th International Conference on ECOMATERIALS, Gifu, November 1999, p. 539.
[14] H. Nishikawa, Y. Takahara, Inorg. Mater. 6 (1999) 291.
[15] Y. Tanaka, private communication.