

Improvement of methyl mercaptan removal by ZnO-coated TiO₂

A. Sakai¹, M. Kanehata¹, T. Ogawa¹ and S. Shiratori^{1,2}

¹Keio University, 3-14-1, hiyoshi, kouhoku-ku, yokohama-shi, 223-0061, Kanagawa
Fax: +81-45-566-1602, e-mail: asa5910@yahoo.co.jp

²SNT, 144-8-O-103, ogura, sachi-ku, Kawasaki-shi, 212-0054, Kanagawa
Fax: +81-44-580-1436, e-mail: shiratori@appi.keio.ac.jp

CH₃SH is listed as one of the causes of a stink and indoor air-pollution. As a method for the removal of CH₃SH, we paid attention to TiO₂ photocatalyst that is harmless and has especially strong oxidation power. The oxidation decomposition of photocatalyst occurs when adsorption occurs, but TiO₂ with the character of acid solid is not necessarily suitable for the adsorption of CH₃SH that is an acid gas. Then, we tried to cover the surface of TiO₂ with ZnO that is a harmless photocatalyst and base solid. We succeeded in coating it by the simple method. As a result, it was confirmed that adsorption ability in the shade place was improved by coating it and the removal performance under the irradiation of 254nm UV lamp was improved, too. When the shape of the surface was observed by using SEM-EDAX, it was confirmed that the surface of TiO₂ was partially covered with ZnO. It was thought that efficient adsorption occurred due to the surface coating, and afterwards photolysis was generated by part of TiO₂ not covered. Therefore, we think that the removal performance is improved by covering TiO₂ with ZnO suitable for the adsorption of CH₃SH that is an acid gas and the rate of the coating is important.

Key words: zinc oxide, titanium dioxide, methyl mercaptan, TiO₂-ZnO

1. INTRODUCTION

Recently, the deterioration of environment has been become a problem. Stink is enumerated as one of the causes of air pollution. Four stinks of ammonia, methyl mercaptan, hydrogen sulfide, and trimethylamine are specified by Environment Agency.

In this study, we paid attention to the removal of methyl mercaptan (CH₃SH) generated from our very familiar ones. CH₃SH is listed as one of the causes of a stink and indoor air-pollution^[1-3]. CH₃SH has an unpleasant smell like a rotten onion, and is a harmful gas that has carcinogenicity in contact with it for a long time. The most important feature is that the sense of smell threshold is very low (0.07ppb). Very low sense of smell threshold requests the removal in a low concentration.

It is titanium dioxide (TiO₂) that has been used to remove it. TiO₂ is a photocatalyst and the reason for its use is (a) because it is white that can be used anywhere, (b) because it stabilizes chemically very much, and is harmless for the living thing, and (c) because it can remove the stench element by strong oxidation power^[4]. Here, the decomposition occurs in the catalyst because adsorption occurs there. Since it was necessary to increase the probability of meeting of the revitalization site on the surface of the catalyst in the removal in a low concentration, we thought that adsorption ability was important. However, it cannot be said that TiO₂ which is an acid solid^[5] is suitable for the adsorption of CH₃SH which is an acid gas^[3].

Then, we tried to coat the TiO₂ surface with zinc oxide (ZnO) to reform the surface. ZnO is also white and a harmless photocatalyst for the living thing, and more importantly it is said that ZnO is a base solid^[6] and suitable for the adsorption of sulfur compound^[7-10].

We succeeded in coating it by the simple method^[11-13]. The LPD (Liquid Phase Deposition) method was used to

coat the surface, and was able to coat it easily at the low temperatures^[14-15].

2. EXPERIMENTAL SECTION

First, 100-ml aqueous solution, which contained 0.01 mol of Zn(NO₃)₂ · 6H₂O (Junsei Chemical Co.,Ltd., 96.0%), 0.02 mol of NH₄Cl (Junsei Chemical Co.,Ltd., 99.0%), 0.01 mol of urea (Junsei Chemical Co.,Ltd., 99.0%), and 5 ml of ammonia solution (Wako Pure Chemical Industries, Ltd., 28~30%) was stirred with magnet stirrer for 1h. 0.7g of TiO₂(P25, Japan Erogel, d=21nm) was added and stirred for 1h. Afterwards, it was put in the plastics container, and was heated at 90°C for 1h and 2h. Thereafter what heated for 1h was written as TiO₂-ZnO① and the for 2h was written as TiO₂-ZnO②. As a comparison, what made only by Zn(NO₃)₂ was prepared. (100ml aqueous solution, which contained 0.01 mol of Zn(NO₃)₂ was stirred with magnet stirrer for 1h and heated at 90°C 1h.) After heating at 90°C, they were filtered while washing it by distilled water (17.1M Ω), and dried for 12h at 90°C. Afterwards, the sample made by only Zn(NO₃)₂ was calcined at 500°C for 4.5h.

The removal performance measurement was done with Gas Chromatograph (G-3900, Hitachi) for TiO₂-ZnO①, TiO₂-ZnO②, TiO₂, ZnO (Wako Pure Chemical Industries, Ltd., d=0.02μm) and two sample made by only Zn(NO₃)₂. The vial container of 100ml was filled with CH₃SH of about 40ppm, and the time when 0.01g of the photocatalyst particle was put into container was assumed to be 0min.

Evaluation of particles was measured using X-ray diffraction (XRD, Rigaku, RAD-C), field emission scanning electron microscope (FE-SEM/EDAX, Hitachi, S-4700). Specific surface area was measured by BET method using ASAP2010 (SHIMADZU).

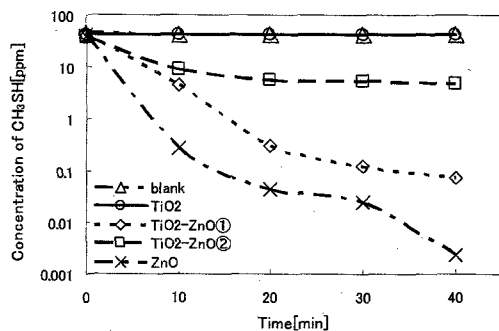


Fig. 1 Removal performance (black)

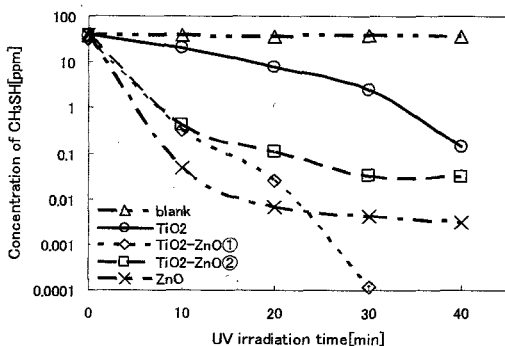
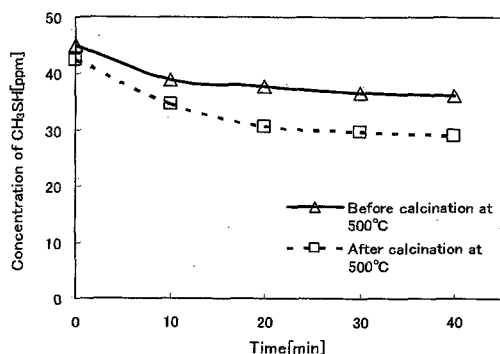


Fig. 2 Removal performance (254nm UV irradiation)

Fig. 3 Removal performance (the sample made by only Zn(NO₃)₂)

3. RESULTS AND DISCUSSIONS

3.1 Removal performance

The result of measuring the concentration attenuation of CH₃SH is shown in Figure 1 (black) and Figure 2 (under the irradiation of 254nm UV lamp). In Figure 1, TiO₂ had hardly any adsorption ability for CH₃SH, whereas ZnO had excellent adsorption for it. Therefore, it was confirmed that the adsorption ability for CH₃SH was improved certainly by coating it with ZnO.

Here, the result of measuring the BET specific surface area is shown in Table 1. There was no large difference in the specific surface area among the particles. Therefore, the improvement of the adsorption ability was considered to be due not to the specific surface area but to the nature of the surface. And the adsorption ability of TiO₂-ZnO ① was higher than that of TiO₂-ZnO ②. This reason is mentioned after.

Table 1. Comparison of specific surface area

Particle	Specific surface area [m ² /g]
TiO ₂	66
ZnO	44
TiO ₂ -ZnO ①	47
TiO ₂ -ZnO ②	55

Moreover, the removal performance of TiO₂ was greatly improved when light was irradiated, but the removal performance of ZnO had hardly changed. This fact is considered to be due to that the oxidation power of TiO₂ photocatalyst is stronger than that of ZnO. In addition, the removal performance of TiO₂-ZnO ① that had higher adsorption ability than TiO₂-ZnO ② was better.

The adsorption ability of the sample made by only Zn(NO₃)₂ is shown in Figure 3. It was understood that adsorption hardly occurred when TiO₂ was only put into the solution of nitrate and then stirred. On the other hand, it was confirmed that the adsorption ability was a little improved by calcinating at 500 °C, but was low, compared with that made by the LPD method. Therefore, the LPD method was considered to be best to coat the surface of TiO₂ with ZnO at low temperatures by the very easy method.

3.2 SEM/EDAX

The result of observing the prepared particles with a SEM is shown in Figure 4. In TiO₂-ZnO ② heated for 2h (Figure 4-c), the rod like a hexagonal column was observed besides a spherical particle. Then, we tried to observe the mapping with EDAX (Figure 5), and it was confirmed the rod was made from only ZnO. In addition, in both TiO₂-ZnO ① and TiO₂-ZnO ②, the TiO₂ surfaces were found to be coated not perfectly but partially, because TiO₂ existed in whole but ZnO existed thinly (Figures 5 and 6).

From the result of Gas Chromatograph and SEM/EDAX, we thought the possibility that the adsorption ability of the rod of ZnO was lower than that of ZnO coating TiO₂. And it was also understood that the efficient adsorption of CH₃SH was generated by ZnO and afterwards photolysis occurred in part of TiO₂ not covered.

3.3 XRD

The result of measurement of XRD is shown in Figure 7. The crystalline of ZnO appeared only in TiO₂-ZnO ②. From this result, it was also understood that the rod observed with a SEM was formed from ZnO. On the other hand, though the peak of ZnO did not appear by heating at 90 °C for 1h, it was thought that TiO₂ was coated by ZnO because the peak of TiO₂ decreased compared with that not coated.

Therefore, the removal performance was improved by coating TiO₂ with ZnO partially, but when heating at 90 °C for a too long time, the rod of ZnO began to be formed, the adsorption ability decreased and the removal performance worsened.

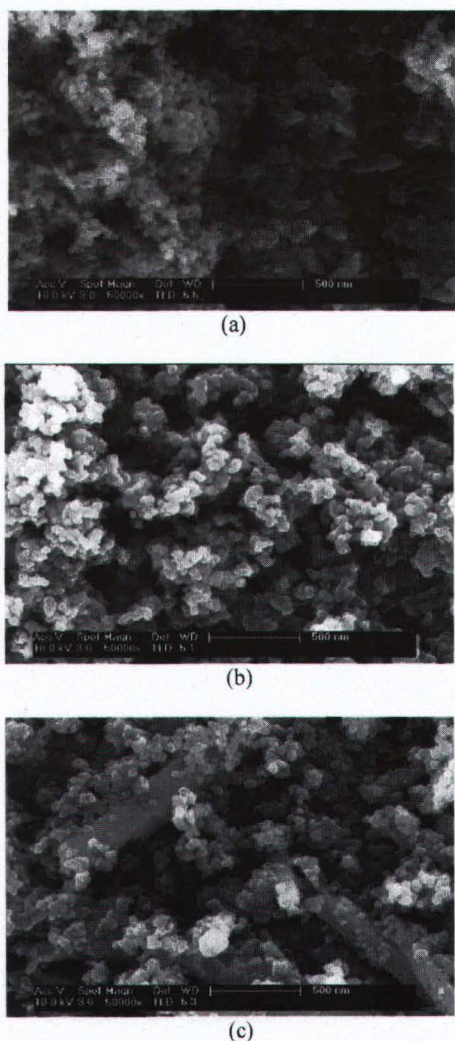


Fig.4 SEM images of (a) TiO₂, (b) TiO₂-ZnO^①, (c) TiO₂-ZnO^②

4. CONCLUSION

We succeeded in covering the surface of TiO₂ with ZnO at low temperatures by very easy synthesis method. The adsorption performance was improved certainly by coating TiO₂ with ZnO. Moreover, the removal performance under the irradiation of light was good when the adsorption ability was high.

From the results of SEM/EDAX, it was understood that ZnO partially covered the surface of TiO₂. The efficient adsorption of CH₃SH was generated by ZnO and afterwards photolysis occurred in part of TiO₂ not covered.

The rod of ZnO appeared besides ZnO that covered the surface when heating it for 2h. As the heating time at 90°C became long, the adsorption ability decreased because the adsorption ability of the rod was worse than that of ZnO which covered TiO₂.

From comparing with the result of the sample prepared by only Zn(NO₃)₂, it was understood that the LPD method was best to coat the surface of TiO₂ with ZnO at low temperatures by very easy method.

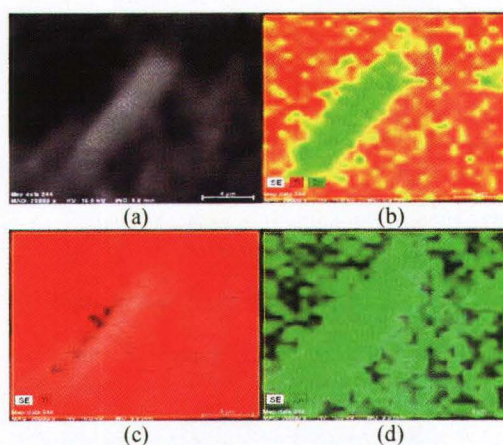


Fig.5 EDAX images of rod: (a) SEM image; (b) mapping of Ti and Zn; (c) mapping of Ti; (d) mapping of Zn

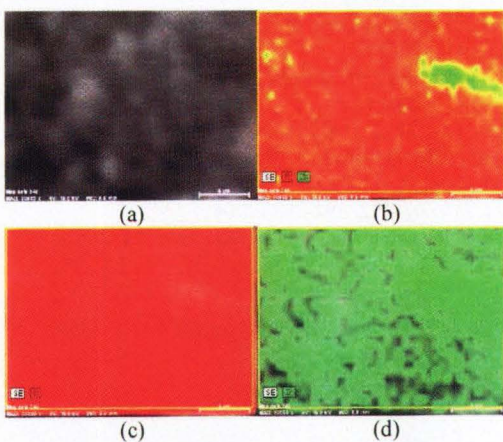


Fig.6 EDAX images of TiO₂-ZnO^①: (a) SEM image; (b) mapping of Ti and Zn; (c) mapping of Ti; (d) mapping of Zn

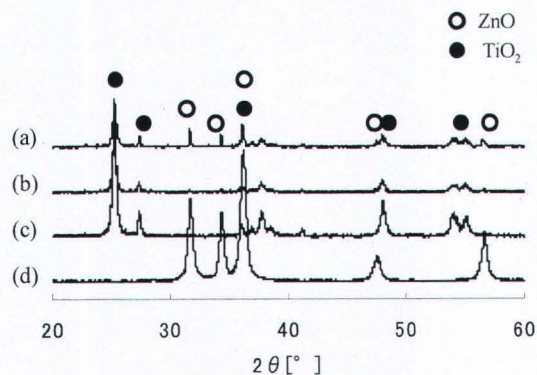


Fig.7 XRD of TiO₂-ZnO^② (a), TiO₂-ZnO^① (b), TiO₂ (c), ZnO (d)

In the future, it will be necessary to examine an increase of the specific surface area and the mechanism of adsorption to improve adsorption ability.

REFERENCES

- [1] T. Oyabu, A. Sawada, T. Onodera, K. Takenaka, B. Wolverton, *Sens. Actuators B*, **89**, 131-136 (2003)
- [2] T. Minamidea, K. Mitsubayashib, H. Saito, *Sen. Actuators B*, **108**, 639-645 (2005)
- [3] X.Z.Li, M.F.Hou, F.B.Li, and H.Chua, *Ind. Eng. Chem. Res.*, **45**, 487-494 (2006)
- [4] N. Watanabe, S. Horikoshi, H. Kawabe, Y. Sugie, H. Hidaka, and J. Zhao, *Chemosphere*, **52**, 851-859 (2003)
- [5] M. Niwa, Y. Habuta, K. Okumura, N. Katada, *Catal. Today*, **87**, 213-218 (2003)
- [6] S. Bancquart, C. Vanhove, Y. Pouilloux, J. Barrault, *Appl. Catal. A Gen.*, **218**, 1-11 (2001)
- [7] J. M. Davidson, C. H. Lawrie, and K. Sohail, *Ind. Eng. Chem. Res.*, **34**, 2981-2989 (1995)
- [8] Elseviers. W, Verelst. H., *Fuel*, **78**, 601-612 (1999)
- [9] J. Dvorak, T. Jirsak and J. A. Rodriguez, *Surf. Sci.*, **479**, 155-168 (2001)
- [10] B. Halevi and J. M. Vohs, *J. Phys. Chem.. B*, **109**, 23976-23982 (2005)
- [11] G. Marci and V. Auguliaro, *J. Phys. Chem.. B*, **105**, 1033-1040 (2001)
- [12] G. Marci and V. Auguliaro, *J. Phys. Chem.. B*, **105**, 1026-1032 (2001)
- [13] S. Y. Jung, H. K. Jun, and S. J. Lee, *Environ. Sci. Technol.*, **39**, 9324-9330 (2005)
- [14] E. Hosono, S. Fujihara, T. Kimura, and H. Imai, *J. Col. Intersrf*, **272**, 391-398 (2004)
- [15] X. Wu, L. Zhemg, and D. Wu, *Langmuir*, **21**, 2665-2667 (2005)

(Received February 16, 2007; Accepted July 12, 2007)