Photocatalytic Degradation of Gaseous Acetaldehyde over Rh-doped SrTiO₃ under Visible Light Irradiation

Yuichi Yamaguchi,^{1,2} Chiaki Terashima,¹ Hideki Sakai,^{1,2} Akira Fujishima,¹ Akihiko Kudo,^{1,3} and Kazuya Nakata*1,⁴

¹*Research Institute for Science and Technology, Photocatalysis International Research Center,*

Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510

²Department of Pure and Applied Chemistry, Faculty of Science and Technology,

Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510

³Department of Applied Chemistry, Faculty of Science, Tokyo University of Science,

1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601

⁴Department of Applied Biological Science, Faculty of Science and Technology,

Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510

(E-mail: nakata@rs.tus.ac.jp)

Rh-doped SrTiO₃ (STO:Rh), a visible-light-driven photocatalyst, was examined for the degradation of acetaldehyde as a volatile organic compound under visible light irradiation. Pristine STO:Rh showed slow degradation of acetaldehyde. After ball milling, the ground STO:Rh had a higher specific surface area than before ball milling, and demonstrated a higher degradation rate for acetaldehyde.

Photocatalytic reactions under light irradiation have gained much attention not only for water splitting for hydrogen fuel production, but also for air and water cleaning.¹⁻⁸ TiO₂ is a material that performs photocatalytic reactions under ultraviolet (UV) light irradiation. However, only 3% of the solar spectrum is composed of UV light. In order to accelerate photocatalytic reactions, the whole range of solar light including visible (vis) should be accessed. Therefore, it is important to develop materials that respond to visible light, comprising 42% of sunlight. Many visible-light-driven photocatalysts have been developed, such as Bi₂WO₆, Bi₂MoO₆, Ag₃VO₄, and BiVO₄, which have demonstrated oxygen evolution from water.⁹⁻¹⁴ Recently, one of the authors reported a unique p-type photocatalyst, rhodium-doped SrTiO₃ (STO:Rh), that was active for hydrogen evolution from water under visible light irradiation.^{15,16} In addition, BiVO₄/STO:Rh composites and photoelectrochemical cells can accomplish water splitting without an external bias under visible light irradiation.^{17,18} Thus, STO:Rh is available for water splitting as a visible-light-driven photocatalyst. The STO:Rh photocatalyst is also active for some organic syntheses such as dehydrogenation of primary alcohols.¹⁹ However, there have been no reports on the capability of STO:Rh for decomposing organic compounds for environmental purification.

In this work, we evaluate the degradation of acetaldehyde, a voltaic organic compound recognized as an origin of the sick building syndrome, using STO:Rh under visible light irradiation. Furthermore, we examined the effect of grinding STO:Rh by ball milling on its activity for acetaldehyde degradation.

STO:Rh was synthesized by a solid-state reaction.¹⁵ A mixture of 17.1 mmol SrCO₃ (Kanto Chemical), 15.8 mmol TiO₂ (Soekawa Chemical Co.), and 0.08 mmol Rh₂O₃ (Wako Pure Chemical) were ground in an alumina crucible with the addition of a small amount of methanol. The mixture was calcined in air at 1173 K for 1 h, then at 1373 K for 10 h. The resulting powder

(1.0 g) was transferred into a 45 mL container with 5.0 mL of ultrapure water and 10 g of zirconia balls (diameter = 1.0 mm). The powder was then milled twice at 800 rpm for 30 min in a ball-milling device (Fritsch: Pulverisette 7). Finally, the ground particles were collected by filtration, washed with ultrapure water, and dried at 60 °C.

The photocatalytic oxidative decomposition of acetaldehyde was examined as follows. A glass petri dish was covered with 0.5 g of STO:Rh in a 500 mL closed glass reactor. The photocatalyst was irradiated at 100 mW cm⁻² light intensity through an L-42 cutoff filter ($\lambda < 420$ nm) using a 200 W Xe lamp. The initial concentration of acetaldehyde was adjusted at 85 ppm. The concentrations of acetaldehyde and carbon dioxide were measured using a gas chromatograph with a flame ionization detector equipped with a methanizer. Acetic acid was detected using high-performance liquid chromatography.

In the X-ray diffraction (XRD) patterns for pristine and ground STO:Rh (Figure 1), peaks of the pristine STO:Rh were assigned to cubic SrTiO₃. After grinding, the crystal phase of STO:Rh was not changed while the full width at half-maximum of the peaks was broadened because the crystalline size was decreased by the ball-milling process.



Figure 1. XRD patterns of (A) pristine and (B) STO:Rh grounded for 60 min.



Figure 2. FE-SEM images of (A) pristine, (B) STO:Rh grounded for 30 min, and (C) STO:Rh grounded for 60 min.

Figure 2 shows field emission scanning electron microscope (FE-SEM) images for pristine and ground STO:Rh. We estimated the specific surface area from nitrogen adsorption at 77 K, using the Brunauer–Emmett–Teller formula. The small specific surface area $(2.6 \text{ m}^2 \text{ g}^{-1})$ and the large particle size $(3-5 \mu\text{m})$ for pristine STO:Rh were due to sintering during high temperature calcination. After ball milling for 30 and 60 min, the surface areas increased significantly to 24 and $46 \text{ m}^2 \text{ g}^{-1}$, respectively, while the particle size decreased to 100–500 nm.



Figure 3. Diffuse reflectance spectra of (A) pristine, (B) STO:Rh grounded for 60 min, and (C) STO:Rh grounded for 30 min.



Figure 4. Photocatalytic degradation of acetaldehyde on (A) pristine, (B) STO:Rh grounded for 30 min, and (C) STO:Rh grounded for 60 min under visible light irradiation ($\lambda > 420$ nm). Photocatalyst: 0.5 g, light source: 200 W Xe lamp with L-42 cutoff filter, gas phase volume: 500 mL.

Diffuse reflectance spectra for pristine and ground STO:Rh showed a broad absorption band around 580 nm, attributed to excitation from the valence band to the Rh⁴⁺ acceptor level (Figure 3). The absorption around 580 nm decreased after ball milling, possibly due to the reduction of Rh⁴⁺ to Rh³⁺ induced by oxygen defects during ball milling to compensate the charge valance. It was suggested with XPS (Figure S1).^{20–23}

We examined the photocatalytic degradation of acetaldehyde by pristine and ground STO:Rh under visible light irradiation (>420 nm), as shown in Figure 4. After equilibrium in the dark for 2 h, the samples were illuminated by visible light (100 mW cm^{-2}) through an L-42 (HOYA: <420 nm) filter from



Figure 5. Photocatalytic degradation of acetaldehyde on ground STO:Rh under visible light irradiation ($\lambda > 420$ nm). Photocatalyst: 0.5 g, light source: 200 W Xe lamp with L-42 cutoff filter, gas phase volume: 500 mL.

a 200 W Xe lamp. The concentration of acetaldehyde (85 ppm) slightly decreased on pristine STO:Rh, whereas it decreased drastically on ground STO:Rh. STO:Rh ground for 60 min showed higher photocatalytic activity than STO:Rh ground for 30 min. It is indicated that the difference in the degradation rate of acetaldehyde between pristine and ground STO:Rh is due to the high specific surface area. To clarify the stability of STO:Rh, we washed the photocatalytic activity after photocatalytic reaction with ultrapure water to remove the acetic acid adsorbed on the surface of STO:Rh. The photocatalytic evaluation was carried out for 5 cycles over STO:Rh ground for 60 min in Figure 5. It was clarified that the photocatalytic activity was quite stable after 5 cycles and washing of STO:Rh, indicating that STO:Rh is reusable.

The turnover number (TON) of reacted acetaldehyde to doped Rh was 2.2, indicating that the degradation of acetaldehyde proceeded photocatalytically, accompanied with electronic excitation from Rh³⁺ of an impurity level in a band gap to the conduction band of SrTiO₃ by visible light illumination. The conduction band level of STO:Rh is about -0.2 V vs. NHE, while the electron donor level in which holes are generated is around 2.2 V.¹² Therefore, oxygen reduction (O₂/HO₂ = -0.13 V vs. NHE, O₂/H₂O₂ = +0.68 V vs. NHE, O₂/H₂O = +1.23 V vs. NHE)²⁴ and acetaldehyde oxidation should simultaneously proceed on the surface of STO:Rh.

We evaluated the amounts of formed carbon dioxide and acetic acid using gas chromatography and HPLC, respectively. As a result, the amounts of formed carbon dioxide and acetic acid were 0.517 and 1.67 μ mol, respectively. The amount of carbon in acetic acid was 3.34 μ mol (1.67 μ mol \times 2). Thus, the total amounts of carbon in carbon dioxide and acetic acid were 3.86 μ mol. The initial concentration of acetaldehyde was 85 ppm, that is, the amount of carbon was calculated to be 3.88 μ mol, indicating that the mass balance of carbon was comparable. It is shown that ground STO:Rh can selectively produce acetic acid by photocatalytic decomposition of acetaldehyde.

Acetic acid was mainly detected rather than CO_2 as an oxidation product of acetaldehyde. The predominant production

of acetic acid is possibly due to the stabilization of acetic acid on the basic surface of STO:Rh and/or the insufficient oxidation potential of holes for complete oxidation to CO_2 .²⁵

In conclusion, STO:Rh prepared by a solid-state reaction was ball milled to increase the specific surface area. Although the concentration of acetaldehyde was slightly decreased using pristine STO:Rh under visible light irradiation, it drastically decreased for ground STO:Rh due to the high specific surface area. Ground STO:Rh showed efficient degradation of acetaldehyde, a volatile organic compound, under visible light irradiation.

This research was partially supported by the Strategic International Research Cooperative Program, Japan Science and Technology Agency (JST).

Supporting Information is available on http://dx.doi.org/ 10.1246/cl.150907.

References

- 1 A. Fujishima, K. Honda, Nature 1972, 238, 37.
- 2 I. Sopyan, M. Watanabe, S. Murasawa, K. Hashimoto, A. Fujishima, J. Photochem. Photobiol., A 1996, 98, 79.
- 3 K. Sunada, Y. Kikuchi, K. Hashimoto, A. Fujishima, *Environ. Sci. Technol.* 1998, 32, 726.
- 4 A. Fujishima, T. N. Rao, D. A. Tryk, J. Photochem. Photobiol., C 2000, 1, 1.
- 5 A. Mills, R. H. Davies, D. Worsley, Chem. Soc. Rev. 1993, 22, 417.
- 6 K. Nakata, A. Fujishima, J. Photochem. Photobiol., C 2012, 13, 169.
- 7 K. Nakata, T. Ochiai, T. Murakami, A. Fujishima, *Electrochim.* Acta 2012, 84, 103.
- 8 A. Fujishima, K. Nakata, T. Ochiai, A. Manivannan, D. A. Tryk, *Interface* **2013**, *22*, No. 2, 51.
- 9 A. Kudo, S. Hijii, Chem. Lett. 1999, 1103.
- 10 Y. Shimodaira, H. Kato, H. Kobayashi, A. Kudo, J. Phys. Chem. B 2006, 110, 17790.
- 11 D. Wang, J. Tang, Z. Zou, J. Ye, Chem. Mater. 2005, 17, 5177.
- 12 R. Konta, H. Kato, H. Kobayashi, A. Kudo, *Phys. Chem. Chem. Phys.* 2003, 5, 3061.
- 13 A. Kudo, Y. Miseki, Chem. Soc. Rev. 2009, 38, 253.
- 14 A. Kudo, K. Omori, H. Kato, J. Am. Chem. Soc. 1999, 121, 11459.
- 15 R. Konta, T. Ishii, H. Kato, A. Kudo, J. Phys. Chem. B 2004, 108, 8992.
- 16 K. Iwashina, A. Kudo, J. Am. Chem. Soc. 2011, 133, 13272.
- 17 Q. Jia, A. Iwase, A. Kudo, *Chem. Sci.* 2014, 5, 1513.
- 18 Q. Jia, K. Iwashina, A. Kudo, Proc. Natl. Acad. Sci. U.S.A. 2012, 109, 11564.
- 19 Z. Liu, J. Caner, A. Kudo, H. Naka, S. Saito, *Chem. -Eur. J.* 2013, 19, 9452.
- 20 Y. Sasaki, H. Nemoto, K. Saito, A. Kudo, J. Phys. Chem. C 2009, 113, 17536.
- 21 Y. Hu, O. K. Tan, J. S. Pan, X. Yao, J. Phys. Chem. B 2004, 108, 11214.
- 22 K. Nomura, K. Tokumistu, T. Hayakawa, Z. Homonnay, J. Radioanal. Nucl. Chem. 2000, 246, 69.
- 23 S. Kawasaki, K. Nakatsuji, J. Yoshinobu, F. Komori, R. Takahashi, M. Lippmaa, K. Mase, A. Kudo, *Appl. Phys. Lett.* 2012, 101, 033910.
- 24 W. Ding, Y. Chen, X. Fu, Appl. Catal., A 1993, 104, 61.
- 25 T. Arai, M. Horiguchi, M. Yanagida, T. Gunji, H. Sugihara, K. Sayama, *Chem. Commun.* 2008, 5565.