Photocatalytic Activities of Rh-doped $CaTiO_3$ under Visible Light Irradiation

Shunsuke Nishimoto, Motohide Matsuda, and Michihiro Miyake*
Department of Environmental Chemistry and Materials, Okayama University,
Tsushima-Naka, Okayama 700-8530

(Received December 15, 2005; CL-051542; E-mail: mmiyake@cc.okayama-u.ac.jp)

The effect of cation substitution into $CaTiO_3$ has been investigated. Rh-doped $CaTiO_3$ showed intense absorption in the visible light region ($\lambda > 420$ nm), and was found to be a new photocatalyst for H_2 evolution from an aqueous methanol solution under visible light irradiation.

Much attention has been paid to photocatalytic water splitting, because the clean energy carrier, H_2, could be obtained from renewable water by solar light.[1] While some ceramic materials reportedly show reasonable activities for splitting water into H_2 and O_2 in a stoichiometric ratio under UV irradiation,[2–11] the number of photocatalytic materials, which are active under visible light irradiation, is still limited. It is, therefore, necessary to develop new type of photocatalytic materials with high activity under visible light irradiation.

Recently, Kudo et al. reported that $SrTiO_3$ doped with noble metal ions such as Ru, Rh, and Ir responded to the visible light and Rh-doped $SrTiO_3$ efficiently produced H_2 from an aqueous methanol solution.[12] When a foreign element is added into some host photocatalysts, the activity generally decreases, compared with those of the undoped materials, because the dopant could provide an electron–hole recombination site. However, this excellent study by Kudo et al. makes us expect that the doping noble metal into the perovskite group is effective for synthesizing new visible light responsible photocatalysts. We have, thus, studied photocatalysts based on $CaTiO_3$, which belongs to the perovskite group and shows H_2 evolution from pure water under UV irradiation,[13] aiming at development of photocatalytic materials under visible light irradiation. In this paper, we report the characteristics of Rh-doped $CaTiO_3$ and its photocatalytic activity of H_2 evolution from an aqueous methanol solution.

Powdered Rh-doped $CaTiO_3$ samples ($CaTi_{1-x}Rh_xO_3$; $0 \leq x \leq 0.03$) were prepared by a conventional solid-state reaction, using $CaCO_3$, TiO_2, and Rh_2O_3 as starting materials. The starting materials were mixed, ground, and then calcinated at 1000 °C for 10 h in the air. After the calcinations, the mixture was reground and fired at 1200 °C for 20 h in the air. The obtained powders were identified by powder X-ray diffraction, using a Rigaku RINT2100/PC diffractometer with monochromated Cu Kα radiation. Diffuse reflectance spectra were measured using a Shimadzu UV-2100PC spectrophotometer. Pt cocatalysts (0.1 wt %) were loaded in situ by a photoreduction method, using an aqueous H_2PtCl_6 solution.

The behavior of photocatalytic H_2 evolution from an aqueous methanol solution was examined using a closed gas-circulation system. The photocatalyst powder (0.3 g) was dispersed in a 10 vol % aqueous methanol solution (150 mL) in a Pyrex-glass cell under an Ar atmosphere. The dispersion was irradiated by a 300-W Xe lamp attached with cut-off filters to control the wavelength of the incident light, and the amount of H_2 was measeured by gas chromatography, using a Shimadzu GC-8A.

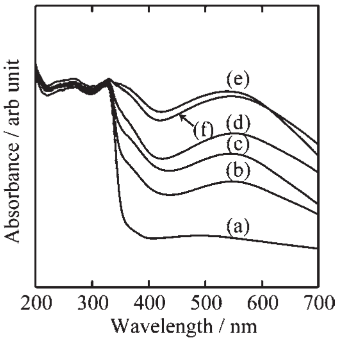

Figure 1. Diffuse reflectance spectra of $CaTi_{1-x}Rh_xO_3$ ($x =$ (a) 0, (b) 0.001, (c) 0.005, (d) 0.01, (e) 0.02, and (f) 0.03).

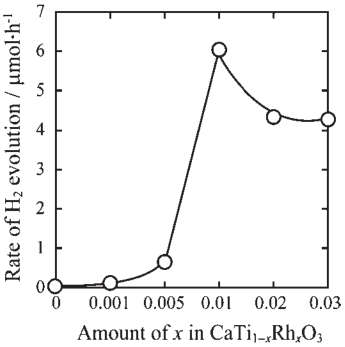

Figure 2. H_2 evolution activity of $CaTi_{1-x}Rh_xO_3$ ($x = 0, 0.001, 0.005, 0.01, 0.02$, and 0.03). Catalyst; 0.3 g, cocatalyst; Pt (0.1 wt %), reactant solution; 150 mL of a 10 vol % aqueous methanol solution, and light source; 300-W Xe lamp with cut-off filters ($\lambda > 420$ nm).

The XRD patterns of $CaTi_{1-x}Rh_xO_3$ samples ($0 \leq x \leq 0.02$) were identified as single phases with orthorhombic system, referring to the previous descriptions on $CaTiO_3$,[14] whereas impurity peaks were observed on the XRD pattern of $CaTi_{0.97}Rh_{0.03}O_3$ sample. It was, thus, considered that Rh could be doped into $CaTiO_3$ up to 2.0 mol %. Figure 1 shows the diffuse reflectance spectra of $CaTi_{1-x}Rh_xO_3$ samples. New absorption peak at about 550 nm appeared by doping Rh in addition to the band gap absorption of $CaTiO_3$. Furthermore, the absorbance of the peak increased with Rh contents up to $x = 0.02$. Consequently, these results indicated that discontinuous levels were formed within the forbidden band by the dopants.

Figure 2 shows H_2 evolution activity of Rh-doped $CaTiO_3$ as a function of doping amount. The H_2 evolution from the aqueous methanol solution under visible light irradiation ($\lambda >$ 420 nm) was observed over Rh-doped $CaTiO_3$, though it was

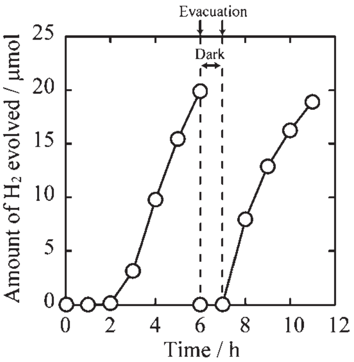

Figure 3. H_2 evolution from an aqueous methanol solution under visible light irradiation over a Pt (0.1 wt %)/$CaTi_{0.99}Rh_{0.01}O_3$ photocatalyst. Catalyst; 0.3 g, cocatalyst; Pt (0.1 wt %), reactant solution; 150 mL of a 10 vol % aqueous methanol solution, and light source; 300-W Xe lamp with cut-off filters ($\lambda > 420$ nm).

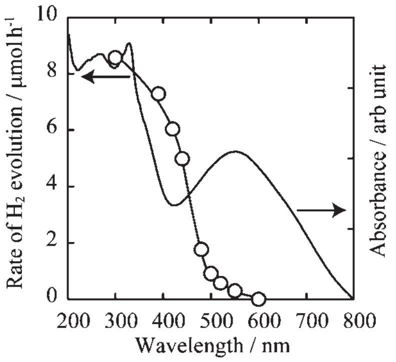

Figure 4. H_2 evolution rate as a function of cut-off wavelength of incident light, and a diffuse reflectance spectrum of $CaTi_{0.99}Rh_{0.01}O_3$. Catalyst; 0.3 g, cocatalyst; Pt (0.1 wt %), reactant solution; 150 mL of a 10 vol % aqueous methanol solution, and light source; 300-W Xe lamp with cut-off filters.

not observed over $CaTiO_3$ without Rh. $CaTi_{0.99}Rh_{0.01}O_3$ sample exhibited the highest H_2 evolution rate. The activity of H_2 production considerably increased with increasing Rh content up to ca. 1.0 mol %. The activity then decreased slowly with further Rh doping. The number of photons absorbed would increase with increasing amount of Rh, resulting in the increase of the activities. On the other hand, the doping a large amount of Rh would facilitate the charge recombination. These conflicting effects in balance, therefore, gave an optimum amount of dopants. Figure 3 shows the time course of H_2 evolution on $CaTi_{0.99}Rh_{0.01}O_3$ sample from an aqueous methanol solution under visible light irradiation ($\lambda > 420$ nm). No reaction took place in the dark. In subsequent reaction after the evacuation, H_2 evolution proceeded again, accompanied by no significant decrease of activity. Moreover, the XRD pattern of the sample after the reaction was same as that before the reaction. These results indicate that $CaTi_{1-x}Rh_xO_3$ samples function as photocatalyst for photoreduction of H^+ into H_2 under visible light irradiation.

It is noted that an induction period was observed at the early stage of the photocatalytic reaction, and the color of the sample changed from grayish purple to yellow after the induction period. The yellow color of the sample returned to the original color as soon as the sample was exposed to the air. Figure 4 shows a diffuse reflectance spectrum of $CaTi_{0.99}Rh_{0.01}O_3$ before the reaction and an action spectrum for H_2 evolution from an aqueous methanol solution. The action spectrum did not correspond to the diffuse reflectance spectrum. That is, H_2 was hardly evolved under the irradiation of light with wavelength beyond 500 nm, though the diffuse reflectance spectrum before the reaction showed absorption peak at about 550 nm. Furthermore, rates of H_2 evolution observed with the cut-off filters of 390, 420, and 440 nm were higher than those expected from the diffuse reflectance spectrum. These phenomena were similar to those of the $SrTi_{1-x}Rh_xO_3$ system in the previous report.[12] Therefore, it was considered that the visible light response was induced by the transition from the electron donor level formed by Rh to the conduction band composed of Ti 3d orbital in $CaTiO_3$.

The H_2 evolution rate of $SrTi_{0.99}Rh_{0.01}O_3$ prepared, referring to the previous report,[12] was measured to evaluate Rh-doped $CaTiO_3$ photocatalyst in this study. As a result, $SrTi_{0.99}Rh_{0.01}O_3$ showed the H_2 evolution rate of 8.48 µmol h^{-1} ($\lambda > 420$ nm) in our measurement system, and this value was estimated to be about 140% that of $CaTi_{0.99}Rh_{0.01}O_3$. Consequently, it was concluded that the doping Rh into the Ca–Ti system perovskite was effective for visible light response, similar to the doping Rh into Sr–Ti system perovskite.

This work was partly supported by The Okayama University 21st Century COE Program "Strategic Solid Waste Management of Sustainable Society."

References

1 A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37.
2 K. Domen, S. Naito, M. Soma, T. Ohnishi, K. Tamaru, *J. Chem. Soc., Chem. Commun.* **1980**, 543.
3 J. Lehn, J. Sauvage, R. Ziessel, L. Halaire, *Isr. J. Chem.* **1982**, *22*, 168.
4 K. Domen, A. Kudo, T. Ohnishi, *J. Catal.* **1986**, *102*, 92.
5 T. Tanaka, K. Shinohara, A. Tanaka, M. Hara, J. N. Kondo, K. Domen, *J. Photochem. Photobiol., A* **1997**, *106*, 45.
6 T. Ishihara, H. Nishiguchi, K. Fukamachi, Y. Takita, *J. Phys. Chem. B* **1999**, *103*, 1.
7 H. Kato, K. Asakura, A. Kudo, *J. Am. Chem. Soc.* **2003**, *125*, 3082.
8 A. Kudo, H. Kato, S. Nakagawa, *J. Phys. Chem. B* **2000**, *104*, 571.
9 M. Machida, J. Yabunaka, T. Kijima, *Chem. Mater.* **2000**, *12*, 812.
10 D. W. Hwang, H. G. Kim, J. Kim, K. Y. Cha, Y. G. Kim, J. S. Lee, *J. Catal.* **2000**, *193*, 40.
11 R. Abe, M. Higashi, Z. Zou, K. Sayama, Y. Abe, *Chem. Lett.* **2004**, *33*, 954.
12 R. Konta, T. Ishii, H. Kato, A. Kudo, *J. Phys. Chem. B* **2004**, *108*, 8992.
13 H. Mizoguchi, K. Ueda, M. Orita, S. C. Moon, K. Kajihara, M. Hirano, H. Hosono, *Mater. Res. Bull.* **2002**, *37*, 2401.
14 L. W. Coughanour, R. S. Roth, S. Marzullo, F. E. Sennett, *J. Research NBS* **1955**, *54*, 149, RP 2576.