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Calcium titanate photocatalyst prepared by a flux method for reduction of carbon dioxide with water

Hisao Yoshida[a,b,*], Like Zhang[c], Masumi Sato[a], Takeshi Morikawa[d], Tsutomu Kajino[d], Takeshi Sekito[e], Shinichi Matsumoto[e], Hirohito Hirata[e]

[a] Kyoto University, Graduate School of Human and Environmental Studies, Kyoto 606-8501, Japan
[b] Kyoto University, Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto 615-8520, Japan
[c] Nagoya University, Graduate School of Engineering, Nagoya 464-8603, Japan
[d] Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan
[e] Toyota Motor Corporation, Toyota 471-8572, Japan

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ABSTRACT

Several calcium titanate samples were prepared by a flux method with various flux salts and various substrate concentration and also by a solid state reaction method. The prepared calcium titanate of various morphologies were loaded with Ag cocatalyst, and examined for the photocatalytic reduction of carbon dioxide with water. A sample prepared with a NaCl flux with a moderate concentration of solute exhibited the highest and stable photocatalytic activity for carbon monoxide production among the prepared samples. It is revealed that the large and flat facets could stabilize the Ag cocatalyst nanoparticles on the surface to enhance the photocatalytic activity for the carbon monoxide production.

1. Introduction

Since we will probably continue to release much carbon dioxide into the atmosphere, we must establish a new technology for the reduction of carbon dioxide in consideration of the carbon cycle on the earth. In order to reduce carbon dioxide chemically, we need a suitable reductant and a suitable catalyst. Although methane or other organic compounds are known as reducing agents, the use of them would substantially involve the emission of carbon dioxide, which seems ineffective. Although hydrogen is a better reductant, at present hydrogen is usually produced from natural gas, which method also produces carbon dioxide eventually [1,2]. The most effective reductant would be water that only releases oxygen after the reaction although the activation of water is usually not easy without consuming energy. It is known that photocatalysis can decompose water molecule to form hydrogen and oxygen at mild condition [3–6], which suggests that the photocatalyst can activate water to promote various reactions without consuming additional energy or reagents by using photoenergy, i.e., solar energy.

As one of the possible and attractive methods, heterogeneous photocatalytic reduction of carbon dioxide with water has been widely studied so far [7–16]. In the 1970s many kinds of photocatalytic systems employing $SrTiO_3$ single crystal, Zn-doped GaP photocathode and predominant semiconductor powders such as TiO_2, ZnO, CdS, GaP and SiC were examined to reduce carbon dioxide with water and some kinds of products were detected [7–9]. In the most of these and subsequent studies, however, the formation of molecular oxygen was scarcely mentioned or much less than the expected quantity although oxygen must be formed as an oxidized product from water [10].

In 1993, Sayama and Arakawa found that ZrO_2 photocatalysts produced hydrogen, oxygen and carbon monoxide from aqueous solution of $NaHCO_3$ and a Cu-loaded ZrO_2 photocatalyst exhibited higher selectivity for the carbon monoxide [11]. In 2011, Kudo and co-workers reported that Ag-loaded $BaLa_4Ti_4O_{15}$ photocatalysts produced these products from aqueous solution in a carbon dioxide flow system [12]. Recently, Ag-loaded Ga_2O_3 photocatalysts have been also studied as similar reaction systems [13–16]. In these photocatalytic systems, the following reactions would take place:

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad (1)$$

* Corresponding author at: Course of Studies on Material Science, Department of Interdisciplinary Environment, Graduate School of Human and Environmental Studies, Kyoto University, Yoshida-nihonmatsu-cho, Sakyo-ku, Kyoto 606-8501, Japan. Tel.: +81 75 753 6594; fax: +81 75 753 2988.
E-mail address: yoshida.hisao.2a@kyoto-u.ac.jp (H. Yoshida).

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$$2H^+ + 2e^- \rightarrow H_2 \quad (2)$$

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \quad (3)$$

In these systems, two reactions, photocatalytic reduction of carbon dioxide to carbon monoxide (Eq. (4)) and photocatalytic water splitting (Eq. (5)), competitively proceeded, where the reaction selectivity varied with the photocatalyst:

$$CO_2 \rightarrow CO + 1/2O_2 \quad (4)$$

$$H_2O \rightarrow H_2 + 1/2O_2 \quad (5)$$

Among the reported photocatalysts, the $Ag/BaLa_4Ti_4O_{15}$ photocatalyst consisted of plate-like particles with anisotropic structure [12], where the reduction to produce carbon monoxide occurred on the Ag cocatalyst located on the edges of the plates while the oxidation would progress on the $BaLa_4Ti_4O_{15}$ surfaces, that is, it is considered that the reaction fields for reduction and oxidation would be separated to contribute to the high photocatalytic performance.

In the present study, in order to discuss the relationship between the morphologic structure of the photocatalyst and the photocatalytic activity for the reduction of carbon dioxide, we employed calcium titanate ($CaTiO_3$) as a semiconductor photocatalyst and a flux method (molten salt method) for the preparation of the photocatalyst. The $CaTiO_3$ photocatalyst have both a conduction band with available potential for reduction of carbon dioxide and a valence bands with enough potential for oxidation of water to oxygen [17]. As for the activation of water, it has already been reported to be photocatalytically active for water splitting [18,19] and photocatalytic steam reforming of methane [19,20]. In addition, the point of zero charge of the $CaTiO_3$ in water is reported as $pH_{PZC} = 3$ [21], i.e., the surface is negatively charged in neutral water, which may be advantageous for adsorption of carbon dioxide also in an aqueous solution. The flux method is expected to provide fine single crystals and thus this method has been applied to synthesize various micro or nano-sized photocatalysts in recent years, for example, many kinds of titanate photocatalysts were synthesized such as $Na_2Ti_6O_{13}$ [22], $Na_2Ti_3O_7$ [23], $K_2Ti_6O_{13}$ [24,25], $SrTiO_3$ [26], $La_2Ti_2O_7$ [27,28], $PbTiO_3$ [29], $CaZrTi_2O_7$ [30] and $AgLi_{1/3}Ti_{2/3}O_2$ [31], although $CaTiO_3$ has not been reported yet. In the present study, we prepared several $CaTiO_3$ samples by a flux method and a conventional solid state reaction method, and examined their photocatalytic performances for the carbon dioxide reduction with water.

2. Experimental

Most of the $CaTiO_3$ samples were synthesized by a flux method from $CaCO_3$ (Kojundo 99.99%) and TiO_2 (rutile, Kojundo 99.9%) as solutes by using $CaCl_2$, KCl or NaCl (Kishida 99.5%) as a flux in the same manner as our previous work [25]. The molar ratio of $CaCO_3$ to TiO_2 was unity, and various concentrations of the solute (x mol% as $CaTiO_3$) in the molten salt mixture were examined, where x was defined as: x [mol%] = (amount of $CaTiO_3$ [mol])/(amount of $CaTiO_3$ [mol] + amount of a flux [mol]) × 100. The mixed starting materials were put into a platinum crucible, which was loosely covered by a lid, heated at a rate of 200 K h^{-1} to 1373 K, held at this temperature for 10 h, and then slowly cooled at a rate of 100 K h^{-1} to 773 K, followed by being naturally cooled to room temperature in an electric furnace. It is considered that the decarbonation of $CaCO_3$ would take place to form CaO species during heating, the mixture of the starting materials would be molten, and then both CaO and TiO_2 clusters in the molten salt would react with each other to form $CaTiO_3$ crystallites during the cooling step. The products were well washed with hot water (353 K) four times to remove the flux. These samples are referred to as CTO(*flux*, *x*), e.g., CTO(NaCl,5). Two samples were prepared by a solid state (SS) reaction method: the same starting materials, $CaCO_3$ and TiO_2, were dried at 383 K, mechanically mixed in a stoichiometric ratio by a wet ball-milling method ($CaCO_3$ 23 g, TiO_2 18.6 g, alumina balls of 1 g and acetone of 80 mL were used) for 24 h, dried in an oven at 343 K overnight, and heated in air atmosphere at 1273 K or 1373 K for 10 h in an alumina crucible. These samples are referred to as CTO(SS, calcination temperature), e.g., CTO(SS,1273 K). Ag cocatalyst of 0.1 or 0.5 wt% (y wt%) was loaded on the surface of the $CaTiO_3$ photocatalysts by a photodeposition method, where methanol of 25 vol% was used as the reductant. The samples are referred to as Ag(y)/CTO, e.g., Ag(0.5)/CTO(NaCl,40).

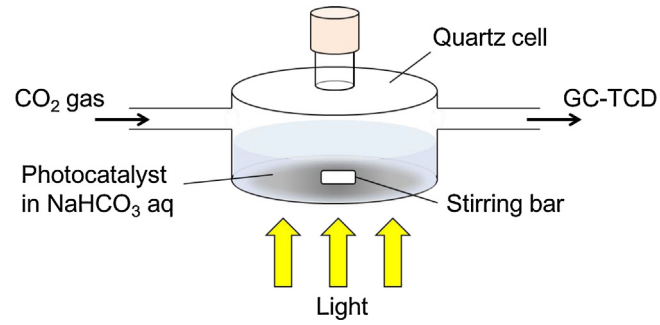

Fig. 1. Photocatalytic reactor for reduction of carbon dioxide with water.

Powder X-ray diffraction (XRD) pattern was recorded at room temperature on a Rigaku diffractometer MiniFlexII/AP using Ni-filtered Cu Kα radiation (30 kV, 15 mA). We used the diffraction line at $2\theta = 33.1°$ to estimate the mean crystallites size of the $CaTiO_3$ samples with Scherrer equation, where a diffraction line of Si powder (Kishida) at 28.5° was used as a reference for the determination of the half maximum full-width. Diffuse reflectance (DR) UV–Visible spectrum was recorded at room temperature on a JASCO V-570 equipped with an integrating sphere covered with $BaSO_4$, where $BaSO_4$ was used as the reference. The bandgap was estimated from the spectra according to Tauc plot [32]. The Brunauer–Emmett–Teller (BET) specific surface area was calculated from the amount of N_2 adsorption at 77 K, which was measured by a Quantachrome Monosorb. Field emission scanning electron microscopy (FE-SEM) images were recorded by a JEOL JSM-7500FA or a Hitachi S-5200. The sizes of particles were measured for around 50 particles by a scale on the SEM images, and the average particle size was determined for each sample.

Photocatalytic reactions were carried out in a specially designed reactor of gas–liquid–solid three phases (Fig. 1) under a flow of CO_2 (Taiyo Nippon Sanso, 99.999%) gas upon photoirradiation from the bottom (16 cm^2) by a 300 W xenon lamp without passing any optical filters, which entirely emitted from UV to visible light, under ambient temperature and pressure. In a quartz cell, 0.2 g of the photocatalyst powder was dispersed in 10 mL of water saturated with 11 mmol of $NaHCO_3$ (Wako, >99.5%). The pH of the solution was 8.3. The mixture of the solution and the photocatalyst powder was photoirradiated with magnetically stirring, where the reaction occurred. The incident light intensity measured in the range of 254 ± 10 nm at the center of the cell was 22 mW cm^{-2}, and the temperature of the reaction cell became 323 K during the photoirradiation. At regular interval (typically every 1 h), the outlet gas was collected in a sampling column and introduced to an online gas chromatograph with a thermal conductivity detector to determine the amount of H_2, O_2 and CO. The production rate of H_2 and CO was precisely determined in this method. The amount of O_2 was determined by the subtraction of the amount of air leak into the system, which sometimes contained large error unfortunately. Other products were not observed in this method. Selectivity for CO in the reduced products, S_{CO} was defined as