



Potassium hexatitanate photocatalysts prepared by a flux method for water splitting



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ABSTRACT

Potassium hexatitanate ($K_2Ti_6O_{13}$) photocatalysts were prepared by a flux method from K_2CO_3 and TiO_2 by using a KCl flux with various concentration of solute and various cooling rate of the molten mixture. A low concentration of the solute and a moderately slow cooling rate provided fine hexagonal rod-like crystals of potassium hexatitanate, which would be formed through dissolution of the solutes in enough amount of the molten salt followed by crystallization and growth of potassium hexatitanate during the cooling step, presumably with fewer defects formation. The fine crystals of potassium hexatitanate loaded with rhodium cocatalyst continuously exhibited the best photocatalytic activity for water splitting among the photocatalysts prepared in this study including a sample prepared by a solid state reaction method.

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1. Introduction

Hydrogen is recognized as a clean energy for environmental concerns since no additional CO_2 is emitted when used. However, we must consider that hydrogen become a truly clean energy only when produced from renewable resources and energies. Photocatalytic water splitting for hydrogen production has been attracted much attention, and many studies have been carried out to develop highly active photocatalysts [1–7].

One of the typical heterogeneous photocatalysts has been a metal oxide semiconductor powder loaded with cocatalyst nanoparticles. It is widely accepted that the photoenergy generates excited electrons and holes in the semiconductor crystallites and a part of them can separately reach the surface of the semiconductor particles to react with molecules or ions. Since the defects and boundaries in the semiconductor are believed to act as recombination centers vanishing the excited electron and hole pairs, the purity and the size of the semiconductor crystallites would be one of the determining factors for the photocatalytic efficiency. On the

other hand, a larger specific surface area of the semiconductor is usually favorable for heterogeneous catalysis since it provides more opportunities for promoting the reaction. Thus, fine single crystals of small size with fewer defects and with a large specific surface area would be ideal for the semiconductor photocatalysts.

Flux method (molten salt method) has been a conventional way to obtain large single crystals [8]. This method is expected to provide fine single crystals of small size depending on the synthesis condition. In principle the crystal growth can proceed in a mixture of solute and molten salt especially during gentle variation of the condition of the molten salt mixture, that is, with decreasing amount of molten salt or temperature to reduce the solubility. If the variation of the condition becomes faster, the size of the obtained crystals would become smaller. Thus, in recent years, this method has been applied to synthesize micro or nano-sized various inorganic crystals as photocatalysts, e.g., TiO_2 [9,10], $Na_2Ti_6O_{13}$ [11–15], $Na_2Ti_3O_7$ [15], $K_2Ti_6O_{13}$ [16], vanadates [17–19], $LaFeO_3$ [20], Nb_2O_5 [21], niobates [22–26], Bi_2MoO_6 [27], $NaTaO_3$ [28], and sulfides [29–31] for degradation of organic dye, volatile organic compounds or fluoroalkylsilane, and $SrTiO_3$ [32], $La_2Ti_2O_7$ [33,34] $PbTiO_3$ [35] $CaZrTi_2O_7$ [36] $AgLi_{1/3}Ti_{2/3}O_2$, $AgLi_{1/3}Sn_{2/3}O_2$ [37], niobates [38–42] tantalates [43–46] and graphitic carbon nitride ($g-C_3N_4$) [47] for water splitting or H_2/O_2 evolution from aqueous solution with a sacrificial reagent. Most of them were well crystallized, and many kinds of crystals showed clear polyhedral structure with some facets [12,14,22–24,28,32,35,45], long structure with

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high aspect ratio [13,15,16,19,26,30] or well-structured surfaces [40–42,46]. It is considered that the crystal having some facets or structured surface would be advantageous for the photocatalytic reaction since the photoexcited electrons and holes generated in the crystallites might go to different surface, which would decrease the frequency of electron–hole recombination [48,49]. Such surfaces would provide the specific reaction fields for either reduction or oxidation, which could decrease the occasion for the reverse reaction to increase the photocatalytic yield. This effect might be important especially in the water splitting since the reverse reaction of water splitting can take place easily.

Potassium hexatitanate ($K_2Ti_6O_{13}$) has been studied as a representative photocatalyst for not only photocatalytic degradation but also water splitting and hydrogen production, e.g., $K_2Ti_6O_{13}$ photocatalysts with RuO_2 or Pt cocatalysts for photocatalytic water splitting [50,51], and those with Rh_2O_3 and Rh cocatalysts for photocatalytic steam reforming of methane [52,53]. However, no study has been reported on the effect of the crystal morphology of the $K_2Ti_6O_{13}$ photocatalyst for the photocatalytic water splitting so far. In the present study, we applied the flux method to prepare several $K_2Ti_6O_{13}$ photocatalysts of various structures or morphology, and discussed relation between the structure and the photocatalytic activity for water splitting.

2. Experimental

Most of samples were prepared in a flux method by reference to a literature [12] from K_2CO_3 (Kishida, 99.99%) and TiO_2 (rutile, Kojundo 99.9%) as starting materials with KCl (Kishida 99.5%) as a flux. These were mixed and put into a platinum crucible. The molar ratio of TiO_2 to K_2CO_3 ($n = TiO_2$ [mol]/ K_2CO_3 [mol]) was 6. Typically, in this method, it is expected that the mixture of the starting materials would be molten at higher temperature and the crystallization of $K_2Ti_6O_{13}$ would take place in the molten KCl during the cooling step. The concentration of $K_2Ti_6O_{13}$ (x mol%) in the molten mixture was varied from 5 to 90 mol%, where x was defined as: x [mol%] = (amount of $K_2Ti_6O_{13}$ [mol]) / (amount of $K_2Ti_6O_{13}$ [mol] + amount of KCl [mol]) \times 100. The temperature of the mixture was increased in an electric muffle furnace with a heating rate of 200 K/h up to 1373 K and maintained for 10 h, where they would be a molten mixture, and then cooled down to 773 K at designated rate ($y = -10$ or -100 K/h), followed by cooling down to room temperature and washing four times with hot water (ca. 353 K, total 1.2 L) to obtain $K_2Ti_6O_{13}$ samples. When a sample was prepared by a rapid cooling ($y = ca. -120,000$ K/h), the hot crucible containing the molten mixture was soaked in water, then the sample was washed with hot water.

Another sample was prepared by a solid state reaction method (SS method). Starting materials, K_2CO_3 (Kishida, 99.5%) and TiO_2 (rutile, Kojundo, 99.9%), were mechanically mixed in a stoichiometric ratio by a wet ball-milling method: alumina balls (150 g, 1 cm in diameter), the starting materials (ca. 24 g), and acetone (75 mL) were put into a capped plastic bottle (300 mL), mixed at 120 rpm for 24 h at room temperature, and dried in an oven at 333 K overnight. The mixed powder was heated in air atmosphere at 1373 K for 10 h in an alumina crucible. After cooling it to room temperature, it was ground by an alumina mortar.

Rhodium cocatalyst (z wt%) was loaded by an oxidative photodeposition method [52,53]. The employed precursors was $RhCl_3 \cdot 3H_2O$ (Kishida, 99%). The $K_2Ti_6O_{13}$ sample (2.0 g) was dispersed into water (360 mL) in a beaker and irradiated from above by using a 300 W xenon lamp, which entirely emitted from UV to visible light (light intensity was 30 mW/cm² when measured at 245 \pm 10 nm in wavelength), for 0.5 h with continuous stirring to clean up the surface of the sample. After introduction of methanol (40 mL) and

the precursor of metal cocatalyst into the beaker and stirring for 1 h, it was irradiated by using the 300 W xenon lamp for 2 h with continuous stirring. In the present condition, the solution would contain a certain amount of dissolved oxygen from the atmosphere. Then, the photocatalyst was separated by suction filtration, washed with distilled water, and dried at 343 K. The powder was granulated to the size of 0.3–0.6 mm for the photocatalytic reaction test. In this paper, the photocatalyst samples prepared by the flux method with parameters, x mol% of the solute, y K/h of the cooling rate and z wt% of the cocatalyst, are denoted to as Rh(z)/KTO(x,y), e.g., Rh(0.003)/KTO(5,–100), while the sample prepared by the SS method was denoted to as KTO(SS).

Powder X-ray diffraction (XRD) pattern was recorded at room temperature on a Rigaku diffractometer MiniFlexII/AP using Ni-filtered Cu K α radiation (30 kV, 15 mA). We used the diffraction line at 29.3 $^\circ$ to estimate the mean crystallites size of the $K_2Ti_6O_{13}$ sample with Scherrer equation since it seemed a clear and intense diffraction line without overlapping the other diffraction lines. Thermogravimetry (TG-DTA) was carried out on a Rigaku Thermo Plus TG8120 from room temperature to 1373 K at the heating rate of 50 K min⁻¹ under a flow of Ar. Diffuse reflectance (DR) UV–visible spectrum was recorded at room temperature on a JASCO V-570 equipped with an integrating sphere covered with BaSO₄, where BaSO₄ was used as the reference. The bandgap was estimated from the spectrum according to Tauc plot [54]. The Brunauer–Emmett–Teller (BET) specific surface area was calculated from the amount of N₂ adsorption at 77 K, which was measured by a Quantachrome Monosorb. Scanning electron microscopy (SEM) images were recorded by a Hitachi S-5200.

Photocatalytic water splitting from pure water vapor was carried out in a fix-bed flow reactor without using any sacrificial reagent. The quartz cell (50 mm \times 20 mm \times 1 mm) [55] was filled with a mixture of the granulated photocatalyst (0.4 g) and quartz granules. The reaction gas, water vapor (1.5%) with argon, was introduced into the reactor at the flow rate of 40 mL/min and the reaction started upon photoirradiation with the 300 W xenon lamp without passing any filters, where the light intensity measured in the range of 254 \pm 10 nm was 10 mW/cm². The temperature of the reaction cell became 308 K during the photoirradiation. At a constant time interval (typically every 30 min), the outlet gas was collected in a sampling column (22.6 mL) and introduced to an online gas chromatographic apparatus with a thermal conductivity detector to determine the amount of H₂ and O₂. The production rate of hydrogen was precisely determined in this method. The formation of oxygen was also clearly observed though the production rate of oxygen could not be accurately determined due to both the low production rate and undesirable small air leak occurring between the sampling column and the gas chromatograph in the present study.

3. Results and discussion

3.1. Characterization

Fig. 1 shows XRD patterns of the prepared samples as well as a calculated one from a database (ICSD #25712). These diffraction patterns of the prepared samples were assignable to that for $K_2Ti_6O_{13}$ and no other diffraction was observed for these profiles, indicating that these samples predominantly consisted of $K_2Ti_6O_{13}$ crystallites. It is interesting that other compounds such as K_2TiO_3 [56], and $K_6Ti_2O_7$ [57] were never detected in these samples even in the presence of excess amount of the KCl flux. The chemical formula of potassium titanate ($K_2Ti_nO_{2n+1}$) was obviously controlled by not the solute concentration (x mol%) in the KCl molten salt but the molar ratio of the starting materials ($n = TiO_2/K_2CO_3$). In the

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