

Granule of potassium hexatitanate fine crystals for photocatalytic steam reforming of methane

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Abstract

Photocatalytic steam reforming of methane (PSRM) can produce hydrogen from methane even at room temperature and thus has been studied recently. In the present study, in order to know the structural aspects affecting the photocatalytic performance, many fine rod-like crystals of potassium hexatitanate ($\text{K}_2\text{Ti}_6\text{O}_{13}$, KTO) were synthesized by a flux method with varying the preparation conditions and examined their photocatalytic activities for the PSRM after loading Rh cocatalyst. It was found that a Rh/KTO fine crystal photocatalyst with larger surface area exhibited the highest hydrogen production rate (up to $30 \mu\text{mol h}^{-1}$) with high selectivity. Further, the granulated crystals exhibited 2.1–2.6 times higher hydrogen production rate than the original powdery fine crystals, suggesting that the physical contact between the fine crystals contributes to the interparticle transfer of the photoexcited carriers and thus enhancing the photocatalytic activity.

Keywords: Potassium hexatitanate; Flux method; Photocatalytic steam reforming of methane; Hydrogen; Granulation.

1. Introduction

Hydrogen is one of the promising and important chemical compounds as a fuel and a chemical feedstock for useful chemicals such as methanol and ammonia. There are several methods to produce hydrogen such as steam reforming of methane [1–6], partial oxidation of methane [7–9], coal gasification [10,11], methane pyrolysis [12–14], water electrolysis [15–17], and so on. As the cheapest route to produce hydrogen, currently, steam reforming of methane (SRM) reaction has become an industrially established system, where the reactants are methane (CH₄), as a main component of natural gas and biogas, and water. The overall chemical equation for this reaction with the successive water gas shift is shown as follows:



This reaction is highly endergonic which requires a tremendous amount of energy to take place, in other words, high reaction temperature is necessary, and thus practically heat from methane combustion is utilized for increasing the temperature in the current SRM, which needs considerable consumption of fossil resource as energy. Further, the high-temperature reaction requires an expensive heat-resistant reactor and careful operation to avoid catalyst deactivation due to coking. Thus, the development of the SRM reaction system that can work at low temperature has been desired.

Photocatalytic reaction system can utilize photoenergy to convert chemical substances. The free and abundance of solar light makes photocatalysis become an attractive method to be developed for many reaction systems. Especially, the use of photoenergy at low temperature for the endergonic SRM reaction is a fascinating

combination. Recently, photocatalytic steam reforming of methane (PSRM) was discovered by employing Pt-loaded TiO_2 [18], and Pt-loaded La-doped NaTaO_3 [18,19]. Afterward, other photocatalysts have been also developed for H_2 production in the PSRM, i.e., Pt-loaded CaTiO_3 [20], Rh-loaded $\text{K}_2\text{Ti}_6\text{O}_{13}$ [21,22], Pt-loaded $\beta\text{-Ga}_2\text{O}_3$ [23], Pt-loaded La-doped CaTiO_3 [24], Rh-loaded $\text{Na}_2\text{Ti}_6\text{O}_{13}$ [25], Rh-loaded TiO_2 [26], Pt-loaded black TiO_2 [27], La-loaded TiO_2 [28], Ag^0/Ag^+ -loaded SrTiO_3 [29], and Pt-loaded YSZ (yttria stabilized zirconia) [30]. Most of the photocatalysts with cocatalyst can utilize light as an energy source and steam (H_2O) as an oxidant to convert methane (CH_4) to H_2 and CO_2 in a molar ratio of $\text{H}_2/\text{CO}_2=4$ even around room temperature although a few photocatalysts can produce CO as a minor product [22,31]. Among these photocatalysts, the Rh-loaded $\text{K}_2\text{Ti}_6\text{O}_{13}$ photocatalyst [21,22] has been the most active photocatalyst in the room temperature PSRM system [22], where the $\text{K}_2\text{Ti}_6\text{O}_{13}$ sample was prepared by a conventional solid-state reaction method.

In general, it has been considered that photocatalyst with less crystal defects provides less recombination of photoexcited electrons and holes to increase the photocatalytic performance, a large specific surface area can provide a large reaction field, and some crystal facets specialized for reductive and oxidative reactions are preferable for the high performance in the photocatalytic reactions. Based on these matters, a flux method has been considered as an advantageous method to obtain such photocatalyst fine crystals since the material can be synthesized in a molten salt to form microcrystals of unique morphology covered with facets with less defects. This method has been used for fabrication of various titanates-based crystals such as $\text{Na}_2\text{Ti}_6\text{O}_{13}$ [25,32,33], $\text{K}_2\text{Ti}_6\text{O}_{13}$ [34–38], and $\text{KTi}_8\text{O}_{16.5}$ [32], $\text{Na}_2\text{Ti}_3\text{O}_7$ [39], $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [40], ATiO_3 (A= Ca, Sr, Ba, and Pb) [24,41–48], $\text{La}_2\text{Ti}_2\text{O}_7$ [49–52], etc. In particular, the fine $\text{K}_2\text{Ti}_6\text{O}_{13}$ crystal, which has

some facets, has been reported as a photocatalyst for water splitting [34,53,54], CO₂ reduction with water [37,38,55], and degradation of various organic contaminants such as methyl orange [56] and amoxicillin [57].

In the present study, we prepared several K₂Ti₆O₁₃ crystals by a flux method in various conditions, loaded Rh cocatalyst on the crystals, and examined them for the PSRM reaction test. As a result, a Rh loaded K₂Ti₆O₁₃ photocatalyst consisting of smaller microcrystals with thinner short facet and higher surface area exhibited higher photocatalytic activity compared to the sample prepared by the conventional solid-state reaction method. In addition, it was found that the granulated photocatalyst exhibited higher activity than the powder sample.

2. Experimental

2.1 Catalyst preparation

Potassium hexatitanate (K₂Ti₆O₁₃, referred to as KTO) was mainly synthesized by a flux method. The typical procedure was as follows. The starting materials, K₂CO₃ (Kishida, 99.9%) and rutile TiO₂ (Kojundo, 99.9%), and a flux such as KCl (Kishida, 99.5%), NaCl (Kishida, 99.5%), or CaCl₂ (Kishida, 95.0%), were physically mixed for 15 min in an alumina mortar. The molar ratio for K₂CO₃ and TiO₂ was always 1:6 while the solute concentration was varied from 10 to 90 mol%. The mixture in a platinum crucible was heated in an electrical furnace, where the temperature was elevated from room temperature to various destined temperature (from 973 K to 1473 K) with an increasing rate (200 K h⁻¹). After holding for 10 h in the temperature, the sample was

cooled down at 100 K h^{-1} to 773 K. The cooling process continued to ambient temperature naturally in the furnace. The product was gently crashed in alumina mortar and washed three times to remove the flux by using hot deionized water (353 K, 500 ml). The filtered sample was then put in an oven at 353 K overnight to remove the remaining water. These samples were referred to as $\text{KTO}(\text{flux},x,y)$, where *flux* shows the used salt such as NaCl, x is the molar ratio of the solute (mol%), and y is the highest temperature (K). After KCl was found to be the most suitable flux, the KCl flux was not indicated in the sample name. A KTO sample was prepared with a short holding time, 1 h instead of 10 h, with a KCl flux at 1173 K (referred to as $\text{KTO}(30,1173)1\text{h}$). Another sample was prepared in the same way by using anatase TiO_2 (Ishihara Sangyo Kaisha, ST-01, $300\text{ m}^2\text{ g}^{-1}$) as a start material instead of rutile TiO_2 with a KCl flux ($\text{KTO}(30,1173)\text{ana}$).

For comparison, a solid-state reaction (SSR) method was used for the preparation of two samples without using any flux, corresponding to $x = 100\%$, at 1173 or 1373 K. The procedure was the same as mentioned above. These samples were referred to as $\text{KTO}(\text{SSR},100,y)$.

Rhodium cocatalyst was loaded on the KTO surface by an impregnation method [22]. Compared to photodeposition method that is often used for photocatalyst, impregnation method would give the same state and the same content of the Rh cocatalyst on each KTO sample regardless the structure and photocatalytic activity, which would be helpful to discuss the differences of the KTO crystals themselves. The KTO samples (1.2 g) were dispersed in a RhCl_3 aqueous solution (Kishida, 99%) (100 ml, 0.03 wt%) and stirred magnetically at 353 K until whole water was evaporated, then dried in the oven at 353 K overnight. The obtained powder sample was mixed carefully for 10 minutes and heated at 773 K for 2 h. The samples are referred to as $\text{Rh/KTO}(x,y)$ for example.

2.2 Characterization

Crystal structure of the KTO samples were evaluated by X-ray diffraction (XRD) pattern measured using a Shimadzu Lab X XRD-6000 at room temperature by using Cu K α radiation (40 kV, 30 mA). Scanning electron microscope (SEM) images of the samples were captured by a JEOL JSM-890. Transmission electron microscopy (TEM) images were taken by a JEOL JEM-2100F at 200 kV. Diffuse reflectance (DR) UV-visible spectra of the samples were measured by a JASCO V-670 where BaSO₄ was utilized as the reference. The Tauc plot was employed to estimated the band gap value [58]. The BET specific surface area was recorded by a Quantachrome Monosorb MS-21 using the amount of N₂ adsorbed on the surface of the sample at 77 K. The Cl concentration remaining on the KTO surface were determined by X-ray fluorescence on an EDX-8000 (Shimadzu).

2.3 Photocatalytic activity tests

Examination of photocatalytic activity of the samples for the PSRM were performed in a fixed bed flow reactor as shown in Fig S1 [19]. A certain amount of Rh/KTO powder was inserted to the Newton press and pressed to become a pellet. The pressure was set to be 40 MPa and held for 1 min before release the pressure. The obtained pellet then crushed by an alumina mortar. To obtained homogeneous granule size, the crashed pellet was screened using 25 and 50-mesh sieves and the granule over the 50-mesh (0.6 g) was introduced to the quartz reactor (60×20×1 mm³) and half occupied the reactor. To perform the reaction, the reactant gas which consisted of CH₄ (25%), H₂O (2.4 %), and argon as carrier were flown in 15 ml min⁻¹. The light was irradiated from a

300 W xenon lamp (PE300BUV) without additional optical filter. The area irradiated by the light was 6 cm². The light intensity used for the reaction was 165 mW cm⁻² when measured in the UV range (254±10 nm). Due to photoirradiation, the temperature of the reactor surface was increased to 323 K. The gaseous products such as H₂ and CO₂ were collected in the sampling loop (18.5 mL) and analysed by an online gas chromatograph equipped with a thermal conductivity detector (Shimadzu, GC-8A, TCD). The interval of every sampling was ca. 30 min. Since the CO₂ sensitivity in the argon carrier gas was low, the experimental error for the determination of CO₂ was relatively large. In this reaction, the ratio of photoexcited electrons and holes consumed for the production, $R(e^-/h^+)$ was calculated according to eq. 2 from the production rates of H₂ and CO₂ as reductive and oxidative products, R_{H_2} and R_{CO_2} , respectively. The value of $R(e^-/h^+)$ should be 1.0 if the reaction take place in a good stoichiometric balance.

$$R(e^-/h^+) = R_{H_2}/(4 \times R_{CO_2}) \quad (2)$$

3. Results and discussion

3.1. Variously prepared KTO photocatalysts

According to the literature [55] but employing a little higher temperature (1373 K), some KTO samples were prepared by the flux method with several fluxes and also the SSR method. Fig. S2 shows the XRD patterns of the KTO(*flux*,50,1373) samples prepared by a flux method with NaCl, KCl, and CaCl₂ fluxes and the KTO(SSR,100,1373) sample prepared by a solid-state reaction method as well as the references. Among them, the KTO(KCl,50,1373) and KTO(SSR,100,1373) samples (Fig. S2 b and d) exhibited the diffraction pattern of K₂Ti₆O₁₃ phase (Fig. S2e) without any other impurity phase. However, XRD patterns of the other two prepared samples seems different from that of

$\text{K}_2\text{Ti}_6\text{O}_{13}$ phase. The pattern of the $\text{KTO}(\text{NaCl}, 50, 1373)$ sample is closer to $\text{Na}_2\text{Ti}_6\text{O}_{13}$ (NTO) or a mixture of NTO and KTO, which is consistent with the previous report [55]. For the $\text{KTO}(\text{CaCl}_2, 50, 1373)$ sample, no diffractions from $\text{K}_2\text{Ti}_6\text{O}_{13}$ phase were detected while TiO_2 rutile and CaTiO_3 were seen as major and minor patterns, respectively (Fig. S2c). This fact revealed that NaCl and CaCl_2 were not suitable for preparing KTO crystals as reported in the previous work [55].

These samples were loaded by 0.03 wt% of Rh-cocatalyst and tested in the PSRM reaction. Fig. 1A representatively shows the time course of the H_2 and CO_2 production rates with the $\text{Rh/KTO}(\text{KCl}, 50, 1373)$ sample in the photocatalytic reaction test for the PSRM reaction. The gas mixture (25% CH_4 , 2.4% H_2O , and 72.6% Ar) was fed at the flow rate of 15 ml min^{-1} around atmospheric pressure and mild temperature. In the initial 1.5 h, the production rate of H_2 gradually increased and became constant to be $16 \mu\text{mol h}^{-1}$ while the production rate of CO_2 was steady in $4 \mu\text{mol h}^{-1}$. The photocatalytic reaction continuously proceeded at least for 4 hours. Other gaseous oxidation products such as ethane and CO was not detected by the online GC–TCD and the ratio of photoexcited electrons and holes consumed for the production was almost unity, $R(e^-/h^+)=1$, suggesting that the products were only H_2 and CO_2 . As the blank tests, the experiments were carried out without light irradiation and without the photocatalyst, which provided no products. These results indicate that the reaction occurred photocatalytically.

Fig. 1B shows the photocatalytic activity of the samples that were prepared by various flux and loaded by 0.03 wt% of Rh-cocatalyst. The highest photocatalytic activity was obtained by the $\text{KTO}(\text{KCl}, 50, 1373)$ sample, indicating that the $\text{K}_2\text{Ti}_6\text{O}_{13}$ crystal without any impurity phases was better for the PSRM reaction. Moreover, the $\text{KTO}(\text{SSR}, 100, 1373)$ sample, prepared by the solid-state reaction, exhibited a bit lower

photocatalytic activity in the PSRM reaction than the KTO(KCl,50,1373) sample, suggesting that the fabrication of the KTO crystal by the flux method contributed to the increase of the activity. On the other hand, the sample prepared by a NaCl flux exhibited lower photocatalytic activity, which would be due to its impurities. In addition, the sample prepared by a CaCl₂ flux, consisting of TiO₂ and CaTiO₃, performed the lowest activity suggesting the KTO phase would contribute to the high performance. For this reason, in the further investigation, only the KCl flux was used for the preparation in the flux method and the flux will be omitted from the sample name.

It is known that the solute concentration in the molten mixture can regulate the growth rate of KTO crystal and change its photocatalytic activity for water splitting, CO₂ reduction, and methane steam reforming [19,24,25,34,55]. Here, in the present work, we prepared various solute concentrations in the KCl flux and investigated the structure and the photocatalytic activity in the PSRM reaction. As shown in Fig. S3A, no impurities were detected in the XRD patterns, which also has been confirmed in the previous reports [34,55]. The difference of intensities in certain 2θ , i.e., 11.5° and 48° (Fig. S3B and C), could be originated from the growth rate difference in the specific facet of the KTO crystal due to the difference of the solute concentration in the molten KCl flux. In contrast, the SEM images (Fig. 2) show that the morphology of the samples was shifted gradually from granular polygonal-like particles to fine and straight long rod-like particles as the solute concentration changed from 100% (without a flux) to 10%. Lower solute concentration provided more molten salt in the mixture which would ease the crystal nuclei to move and growth in the certain direction according to the crystal habit of K₂Ti₆O₁₃. As a result, the KTO crystal obtained in lower solute concentration has larger and longer particle as well as finer facets. By TEM measurement of the Rh/KTO(10,1373) sample, a rod-like

particle was observed with a length of ca. 1 μm , which is consistent with the SEM image (Fig. 2e). The electron diffraction of the KTO particle provided a single diffraction pattern (Fig. 3B) in several spots. This result indicates that the observed rod-like particle was a single crystal.

Fig. 4 shows the photocatalytic activities of these samples. As shown, the photocatalytic activity was varied with the difference of the solute concentration and the highest production rates of H_2 and CO_2 were obtained by the sample prepared with the lowest solute concentration, i.e., the Rh/KTO(10,1373) sample. These results indicate that the proper morphology was an essential factor in enhancing photocatalytic activity.

However, it is well known that the photocatalyst structural properties such as surface area, crystal size, and so on were also considered as the essential factors to affect the photocatalytic activity. Thus, to investigate more profoundly, the effects of the heating temperature and the solute concentration were investigated with the KTO(10,y) and KTO(x,1173) samples. No impurity phases in the XRD patterns were found for the entire KTO(10,y) and KTO(x,1173) samples (Fig. S4). The morphology also did not change with varying the heating temperature (Fig. S5). On the other hand, the crystal size and specific surface area changed (Table 1, entries 1,4,7,10–13).

Fig. 5 shows the photocatalytic activities and the specific surface area of these samples. The photocatalytic activity of various Rh/KTO(10,y) samples were similar except for the Rh/KTO(10,1473) sample (Fig. 5A). The low activity of the Rh/KTO(10,1473) sample could be corresponded to the low specific surface area, i.e., a decrease of the active sites for the reaction, or the possible presence of small amount of TiO_2 or defects due to evaporation of potassium at high temperature [55]. However, the sample prepared in 1373 K performed similar activity with the higher surface area

samples such as the Rh/KTO(10,1173) and Rh/KTO(10,1273) samples even the specific surface area was small. Other parameters compensating the low surface area, such as crystal growth, should also affect the photocatalytic activity since the surface area could not independently explain the phenomena. In the previous study, it was suggested that larger fine crystal size of the photocatalysts such as NaTaO₃ and Na₂Ti₆O₁₃ performed higher photocatalytic activity in the PSRM due to the well-grown crystals that would have less crystal defects and large photoabsorption area [19,25]. Thus, in the present study, even the surface area of the KTO(10,1373) sample was lower than the KTO(10,1173) and KTO(10,1273) samples, the well-grown crystals at moderate temperature compensated the decrease of the photocatalytic active sites. The result indicated that the completeness of crystals and high surface area can contribute to the photocatalytic activity.

On the other hand, when the solute concentration was varied in the lower heating temperature such as 1173 K, the trend of the photocatalytic activity was different from that over the samples prepared at higher heating temperature such as 1373 K, i.e., the highest H₂ and CO₂ production rates were obtained by the Rh/KTO(30,1173) sample as shown in Fig. 5B. The surface area or the proper morphology could be considered as the vital factor for enhancing the photocatalytic activity in the samples prepared at lower temperature. Thus, another series of the KTO(30,y) samples were further prepared for searching the optimum photocatalytic activity of the Rh/KTO photocatalysts by varying the heating temperature, holding time, and different TiO₂ precursors.

The Rh/KTO(30,y) samples were prepared at lower heating temperature such as 973–1273 K. As shown in Fig. S6, except the KTO(30,973) sample, no other impurity phases were recorded in the diffractograms. Some TiO₂ rutile peaks were recorded for the KTO(30,973) sample. Since the melting point of pure KCl is 1043 K, the crystal growth

of KTO was not completed at 973 K in the present conditions, consisting with literatures [34,59] while the precursors were wholly transformed to KTO at 1073 K. The structural properties are listed in Table 1, entries 6–9. The photocatalytic activity and the specific surface area of these Rh/KTO(30,y) samples are depicted in Fig. 6a–d. As shown, the photocatalytic activity of the Rh/KTO(30,1073) sample (Fig. 6a) are similar to that of the Rh/KTO(30,1173) sample (Fig. 6b) even the specific surface area was different. Higher surface area provided more active sites but at the same time smaller crystal size also would give more surface defect sites that reduce the photocatalytic activity. Moreover, the samples prepared at higher temperature such as the Rh/KTO(30,1273) and Rh/KTO(30,1373) samples (Fig. 6c and d) exhibited lower activity probably due to their very low surface area.

In the previous report, it was suggested that the appropriate holding time could provide well formed KTO crystal and shorter heating time such as 1 h was not enough to synthesized the pure KTO [55]. However, in the present experiment, the result seems to be different probably due to the detailed conditions such as different crucible used and mixing preparation as mentioned before. For the sample with a short time holding temperature, i.e., the KTO(30,1173)1h sample, the KTO crystal still also formed well (Fig. S6d), which was the similar crystal size to the KTO(30,1173) sample in the standard conditions (10 h holding at 1173 K) as shown in the Table 1, entries 7 and 14. The photocatalytic performance of the KTO(30,1173)1h sample was also similar to the KTO(30,1173) sample (Fig. 6 b and e). These facts indicate that such a short holding time was enough to synthesize potassium hexatitanate even at lower temperature, i.e., 1173 K. This result also revealed that the heating duration more than 1 h in the molten flux was not an essential factor for nucleation and crystal growth of KTO. The crystal size should

be determined by the other variables such as the cooling rate.

As shown in Table 1, entries 7 and 15, the KTO(30,1173) samples prepared from different TiO₂ polymorphs, it was obvious that the crystal size of the sample prepared from TiO₂ anatase was bigger than that from rutile even though the anatase precursor has much smaller particles; the specific surface area of anatase and rutile samples used here were 300 and 2.5 m² g⁻¹, respectively. Since TiO₂ anatase in the KCl flux might be more reactive than rutile one, the crystal growth with the anatase precursor would be well enhanced, resulting a bigger crystal size. Wang et al. reported that potassium hexatitanate whisker could be perfectly produced through a hydrothermal method in the lower temperatures around 523 K by utilizing TiO₂ anatase as starting material while from TiO₂ rutile it was only partially produced [60]. Fujiki and Izumi reported that KTO fiber which was synthesized in tungsten flux method using smaller anatase particles as the precursor, was longer than that prepared from the rutile-TiO₂ precursor of larger particle size [61]. The same effect might occur in the present case using the KCl flux. The present result was opposite to the case of the previous study on sodium titanate [33], i.e., smaller rod sodium titanate crystal was produced by utilizing TiO₂ anatase (300 m² g⁻¹) compared to rutile (2.5 m² g⁻¹) precursor. This crystallization chemistry requires more systematic study. As for the photocatalytic activity (Fig. 6 b and f), the sample prepared from anatase exhibited lower activity, which would be originated from larger crystal size and lower specific surface area.

The effect of the rhodium cocatalyst loading was also confirmed by using the KTO(SSR,100,1373) sample. The production rates of H₂ and CO₂ with the bare KTO(SSR,100,1373) sample was 0.3 and 0 μmol h⁻¹, respectively (Table 1 entry 16). As shown, the Rh/KTO(SSR,100,1373) sample produced H₂ with the production rate of 13

$\mu\text{mol h}^{-1}$ (Table 1 entry 2), which is more than 40 times higher than the bare KTO(SSR,100,1373) sample. The presence of Rh cocatalyst on the surface is considered to enhance the charge separation thus increase photocatalytic activity [22,25].

In the present study, chloride salt and RhCl_3 were used for the sample preparation. Since residual Cl anion may affect the photocatalytic activity, we measured the Cl content in the representative samples by using XRF measurement and the results are shown in the Table S1. The presence of Cl anion was elucidated on some of the samples although the concentrations were very low. As a result, no clear relationship between the Cl content and the photocatalytic activity was noticed, suggesting that the influence of the residual Cl anions on the photocatalytic activity should be very limited.

Among the $\text{Rh/KTO}(x,y)$ samples listed in Table 1, the samples, $\text{Rh/KTO}(50,1173)$, $\text{Rh/KTO}(30,1173)$, $\text{Rh/KTO}(30,1173)1\text{h}$, and $\text{Rh/KTO}(30,1073)$, showed almost similar photocatalytic activity with the highest H_2 production rate such as 29, 30, 29, and 29 $\mu\text{mol h}^{-1}$, respectively. Among them, the $\text{Rh/KTO}(30,1173)$ sample gave the highest activity, i.e., the methane conversion was 0.081% and the apparent quantum efficiency was 0.15%.

3.2. Relation between structure and photocatalytic activity

Here, the photocatalytic activity of the two series of the prepared samples will be discussed, i.e., the $\text{Rh/KTO}(x,1173)$ and $\text{Rh/KTO}(x,1373)$ samples, which were prepared with various solute concentrations in the molten mixture with a KCl flux. As shown in Fig. S7, among the $\text{Rh/KTO}(x,1173)$ samples the suitable solute concentration was 30–50%; the $\text{Rh/KTO}(30,1173)$ and $\text{Rh/KTO}(50,1173)$ samples exhibited the highest photocatalytic activities. On the other hand, in the higher heating temperature at 1373 K, the most active sample was the $\text{Rh/KTO}(10,1373)$ sample prepared with the low solute

concentration. These results indicate that the solute concentration could affect the photocatalytic activity of KTO samples. When high heating temperature (1373 K) was applied, the lower solute concentration produced finer KTO crystals thus enhance the photocatalytic activity. In contrast, when the low heating temperature utilized, the other structural properties such as surface area and the crystal thickness gave more impact to control the photocatalytic activity compared to the fine crystals. Thus, it is proposed that the solute concentration could regulate the photocatalytic activity of the sample by control the structural properties of KTO, but the other factors also must be considered.

Furthermore, the heating temperature also seems to have a critical effect on enhancement of photocatalytic activity. As shown in Table 1, the Rh/KTO(30,y) samples prepared at lower temperatures, i.e., Rh/KTO(30,1073) and Rh/KTO(30,1173), exhibited better photocatalytic activity compared to the others such as Rh/KTO(30,1273) and Rh/KTO(30,1373). The lower heating temperature produced smaller crystal size, shorter rod crystal, thinner short facet, and thus higher specific surface area. To further investigate the critical parameters in the PSRM, the H₂ formation rate was plotted against some parameters (Fig. S8). The specific surface area had a moderately positive correlation to photocatalytic activity, while crystal thickness had a negative one. Since the increase in thickness would lead to a decrease in the specific surface area, it would be reasonable to consider that a larger surface area gives the larger adsorption of substrates and thus increases the rate of H₂ production. Our group previously reported that smaller potassium hexatitanate crystals could produce more H₂ in overall water splitting by UV-light, which is a similar trend to the present work [34]. On the other hand, in the present reaction system, the H₂ production rates differed by a factor of up to two for the samples with similar specific surface areas, strongly suggesting that other parameters such as crystal

length and crystal thickness also affect catalytic performance (Fig. S8) since the long and short facets contribute to the reductive and oxidative reactions, respectively [38].

3.3. Effect of granulation

In the present system using a fixed bed reactor, first a powdery photocatalyst sample consisting of micrometer-sized fine crystals was conventionally pressed under 40 MPa and then crashed into millimetres-sized granules (25–50 mesh) before introducing it to the reactor. The granule form can help us to introduce the photocatalyst into the thin reaction cell and realize the smooth gas flow in the reaction cell. However, one may consider that the pressing and crashing might make some damages on the KTO fine crystals, which might produce many cracks and defects and enhance the recombination of the photoexcited electrons and holes. Thus, in the present study, the Rh/KTO granule samples prepared by pressing at various pressures from 20–60 MPa were compared with the original powder sample. Although the required weight to fill the reactor was different between the granule and powder samples, the photo-irradiated area was arranged to be the same as the usual conditions to be 6 cm². Fig. 7 shows the relationship between pressures to prepare the granules and the H₂ formation rate. In powder form, the H₂ production rate was relatively low (9.2 μmol h⁻¹). On the other hand, the photocatalytic performance increased significantly by 2.1–2.6 times by making the granules at a pressure of 20–60 MPa compared to the original powder sample. By pressing at higher pressures, the amount of the KTO photocatalyst in the reactor increased (Table S2). To investigate the effect of the sample amount on the photocatalytic activity, the H₂ formation rate was divided by the sample weight and plotted with the pressure (Fig. S9). The H₂ formation

rate per weight on the granule sample were higher than that on the original powder one by 1.3–1.5 times. The advantage of the granule sample was also confirmed even when the activity was divided by the sample amount. Note that there would be no large difference in the number of the absorbed photons between the powder and granule KTO samples because KTO samples had similar absorption properties and no light was transmitted through the sample due to the absorption and scattering by the samples. To investigate the effect of the sample amount in detail, the photocatalytic activity of the KTO samples diluted by quartz sands was investigated, where the quartz sands were selected as a diluent because it is transparent to UV light and inactive for the PSRM reaction. In this experiment, the irradiation area was arranged to be 6.0 cm² as in the above case. The photocatalytic activity was almost the same as the original one, even by decreasing the amount of KTO to 35wt% (Table S3). This result suggested that the number of absorbed photons is not changed largely by the dilution of the quartz and the irradiated photon number almost determined the H₂ formation rate. More importantly, the amount of the photocatalysts has no significant effect on the photocatalytic activity in the present conditions, also suggesting that the sample amount would not affect the photocatalytic activity largely in the comparison between powder and granule samples. Pressing would increase the contact between the KTO crystals based on the SEM images of the granule sample (Fig. 8). The increased contact might have a positive effect on the photocatalytic activity possibly due to the improved interparticle electron transfer as illustrated in Fig. 9.

3.3. Reaction mechanism

Here is the proposed reaction mechanism of the PSRM over the Rh/KTO

photocatalyst. First, the light is absorbed by the KTO crystals and photoexcited electrons and holes are produced. Then, the charge carriers migrated to the photocatalyst surface. Although the charge carriers recombined during transportation to the crystal surface in large portion, some of them can reach the surface and react with the reactants. The water and methane on the Rh/KTO surface would be activated by the holes to produce protons and radical surface intermediates such as methyl radicals and OH radicals [62]. The methyl radicals would successively react with water or OH radicals to produce CO₂ while electrons would reduce the protons to H₂. In the case of the granule sample of Rh/KTO, the electrons can transport more easily between the particles than the powder sample, which might contribute to the effective charge separation and high photocatalytic activity.

4. CONCLUSIONS

Many rod-like fine KTO crystals covered with facets having various structural aspects were successfully synthesized by employing the flux method. The photocatalytic activity of the Rh/KTO samples varied with the KTO structure. The KTO crystals with larger surface area exhibited higher photocatalytic activity for the PSRM in the present conditions. Other factors such as crystal thickness also influenced on the photocatalytic activity. Among them the KTO(30,1173) sample prepared by rutile-TiO₂ precursor and KCl flux at 1173 K exhibited the highest photocatalytic activity after loading Rh cocatalyst. Furthermore, it was found that the granule of the Rh/KTO fine crystal sample showed 2.1-2.6 times higher activity than the original powdery fine crystals, which would result from the better intraparticle contact due to the pressing the fine crystals to get the granule form. Further optimization on the cocatalyst and the loading method would contribute to further development of the KTO photocatalyst.

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LIST OF TABLE AND FIGURES.

Table 1. Structural and optical properties of the prepared samples and their photocatalytic activity in the PSRM reaction.

Fig. 1. (A) Time course of the production rates of H₂ (filled circle) and CO₂ (filled squares) over the Rh/KTO(KCl,50,1373) sample. (B) Production rates of H₂ (white bar) and CO₂ (black bar) in the PSRM, and the consumed electron/hole ratio calculated from the production rates, $R(e^-/h^+)$ (open triangle), over the prepared KTO(flux,50,1373) and KTO(SSR,100,1373) samples, (a) KTO(NaCl,50,1373), (b) KTO(KCl,50,1373), (c) KTO(CaCl₂,50,1373), and (d) the KTO(SSR,100,1373) sample. The photocatalyst granule used was 0.6 g. The reactant gas mixture (25% CH₄, 2.4% H₂O, and 72.6% Ar) was introduced at the flow rate of 15 ml min⁻¹. The irradiation area was 6.0 cm². The light intensity used was 165 mW cm⁻² when measured at 254±10 nm in wavelength. Products were sampled at 4 hours later after starting photoirradiation.

Fig. 2. SEM images of various Rh/KTO(*x*,1373) samples, where *x* was the solute concentration in mol.%, (a) Rh/KTO(SSR,100,1373), (b) Rh/KTO(90,1373), (c) Rh/KTO(50,1373), (d) Rh/KTO(30,1373), and (e) Rh/KTO(10,1373).

Fig. 3. (A) TEM image and (B) electron diffraction pattern of the Rh/KTO(10,1373) sample.

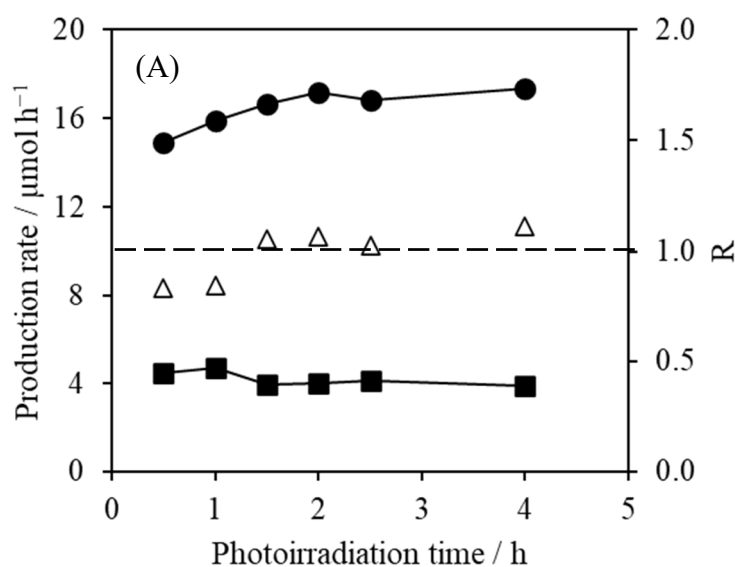
Fig. 4. Production rates of H₂ (white bar) and CO₂ (black bar) in the photocatalytic reaction test for the PSRM reaction, and the consumed electron/hole ratio calculated from the production rates, $R(e^-/h^+)$ (open triangle), over the Rh/KTO(*x*,1373) samples. The reaction conditions are the same as those mentioned in the caption of Fig. 1.

- Fig. 5.** Production rates of H₂ (white bar) and CO₂ (black bar), and the specific surface area (filled triangle) of (A) various Rh/KTO(10,y) samples and (B) various Rh/KTO(x,1173) samples. The reaction conditions are the same as those mentioned in the caption of Fig. 1.
- Fig. 6.** Production rates of H₂ (white bar) and CO₂ (black bar), and the specific surface area (filled triangle) of the Rh/KTO(30,y) samples, (a) Rh/KTO(30,1073), (b) Rh/KTO(30,1173), (c) Rh/KTO(30,1273), (d) Rh/KTO(30,1373), (e) Rh/KTO(30,1173)1h, and (f) Rh/KTO(30,1173)ana. The reaction conditions are the same as those mentioned in the caption of Fig. 1.
- Fig. 7.** H₂ production rate of the powder (0 MPa) and granule (20-40 MPa) Rh/KTO(10,1373) samples. The reactant gas mixture (25% CH₄, 2.4% H₂O, and 72.6% Ar) was introduced at the flow rate of 15 ml min⁻¹. The irradiation area was 6.0 cm². The light intensity used was 165 mW cm⁻² when measured at 254 ± 10 nm in wavelength. Products were sampled at 3 hours later after starting photoirradiation.
- Fig. 8.** SEM images of the granule Rh/KTO(10,1373) sample.
- Fig. 9.** Illustrations of the Rh/KTO samples consisting of (a) the powdery fine crystals, and (b) the granulated fine crystals for the PSRM.

Table. 1 Structural and optical properties of the prepared samples and their photocatalytic activity in the PSRM reaction

Entry	Sample	Crystal size (SEM) ^{a/} μm		Aspect ratio ^b	$S_{\text{BET}}^{\text{c}} /$ $\text{m}^2 \text{h}^{-1}$	Band gap ^{d/} eV	Production rate ^{e/} $\mu\text{mol h}^{-1}$		$R(\text{e}^-/\text{h}^+)^{\text{f}}$
		Length (long side)	Thickness (short side)				H_2	CO_2	
1	Rh/KTO(SSR,100,1173)	0.90	0.62	1.4	4.0	3.33	21	5.5	1.0
2	Rh/KTO(SSR,100,1373)	1.12	0.79	1.4	2.5	3.31	13	3.1	1.1
3	Rh/KTO(90,1373)	1.36	0.69	2.0	5.1	3.33	12	3.5	0.9
4	Rh/KTO(50,1173)	0.85	0.21	4.1	10.2	3.36	29	7.1	1.0
5	Rh/KTO(50,1373)	1.52	0.49	3.1	6.2	3.34	17	3.9	1.1
6	Rh/KTO(30,1073)	0.64	0.09	7.0	16.1	3.35	29	7.1	1.0
7	Rh/KTO(30,1173)	0.95	0.19	5.1	13.3	3.35	30	7.5	1.0
8	Rh/KTO(30,1273)	1.96	0.45	4.3	5.4	3.35	18	5.3	0.9
9	Rh/KTO(30,1373)	2.81	0.49	5.7	5.2	3.34	12	3.3	0.9
10	Rh/KTO(10,1173)	2.13	0.24	8.8	10.7	3.33	23	5.7	1.0
11	Rh/KTO(10,1273)	2.08	0.32	6.5	9.3	3.37	23	6.7	0.9
12	Rh/KTO(10,1373)	4.58	0.59	7.8	5.4	3.32	23	6.1	0.9
13	Rh/KTO(10,1473)	5.22	0.74	7.1	4.3	3.29	14	4.2	0.8
14	Rh/KTO(30,1173)1h	0.93	0.16	5.8	13.2	3.35	29	6.6	1.1
15	Rh/KTO(30,1173)ana	1.64	0.21	7.7	11.0	3.36	19	4.4	1.1
16	KTO(SSR,100,1373)	1.12	0.79	1.4	4.0	3.31	0.3	n.d	—

^a Average crystal size measured from the SEM images. ^b Aspect ratio calculated from dividing length/thickness. ^c Specific surface area measured by a BET method. ^d Band gap calculated from the DR UV-Vis spectra. ^e Sampling was carried out 4 hours later after starting irradiation. ^f Ratio of electrons and holes consumed for the products formation.



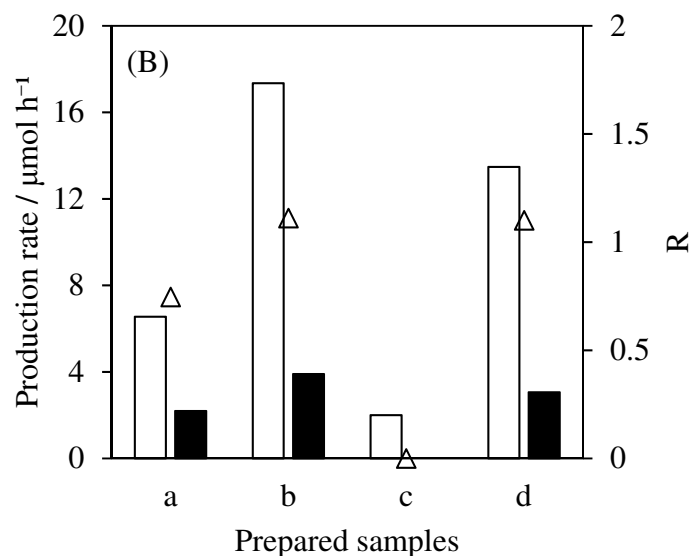


Fig. 1. (A) Time course of the production rates of H₂ (filled circle) and CO₂ (filled squares) over the Rh/KTO(KCl,50,1373) sample. (B) Production rates of H₂ (white bar) and CO₂ (black bar) in the PSRM, and the consumed electron/hole ratio calculated from the production rates, $R(e^-/h^+)$ (open triangle), over the prepared KTO(flux,50,1373) and KTO(SSR,100,1373) samples, (a) KTO(NaCl,50,1373), (b) KTO(KCl,50,1373), (c) KTO(CaCl₂,50,1373), and (d) the KTO(SSR,100,1373) sample. The photocatalyst granule used was 0.6 g. The reactant gas mixture (25% CH₄, 2.4% H₂O, and 72.6% Ar) was introduced at the flow rate of 15 ml min⁻¹. The irradiation area was 6.0 cm². The light intensity used was 165 mW cm⁻² when measured at 254±10 nm in wavelength. Products were sampled at 4 hours later after starting photoirradiation

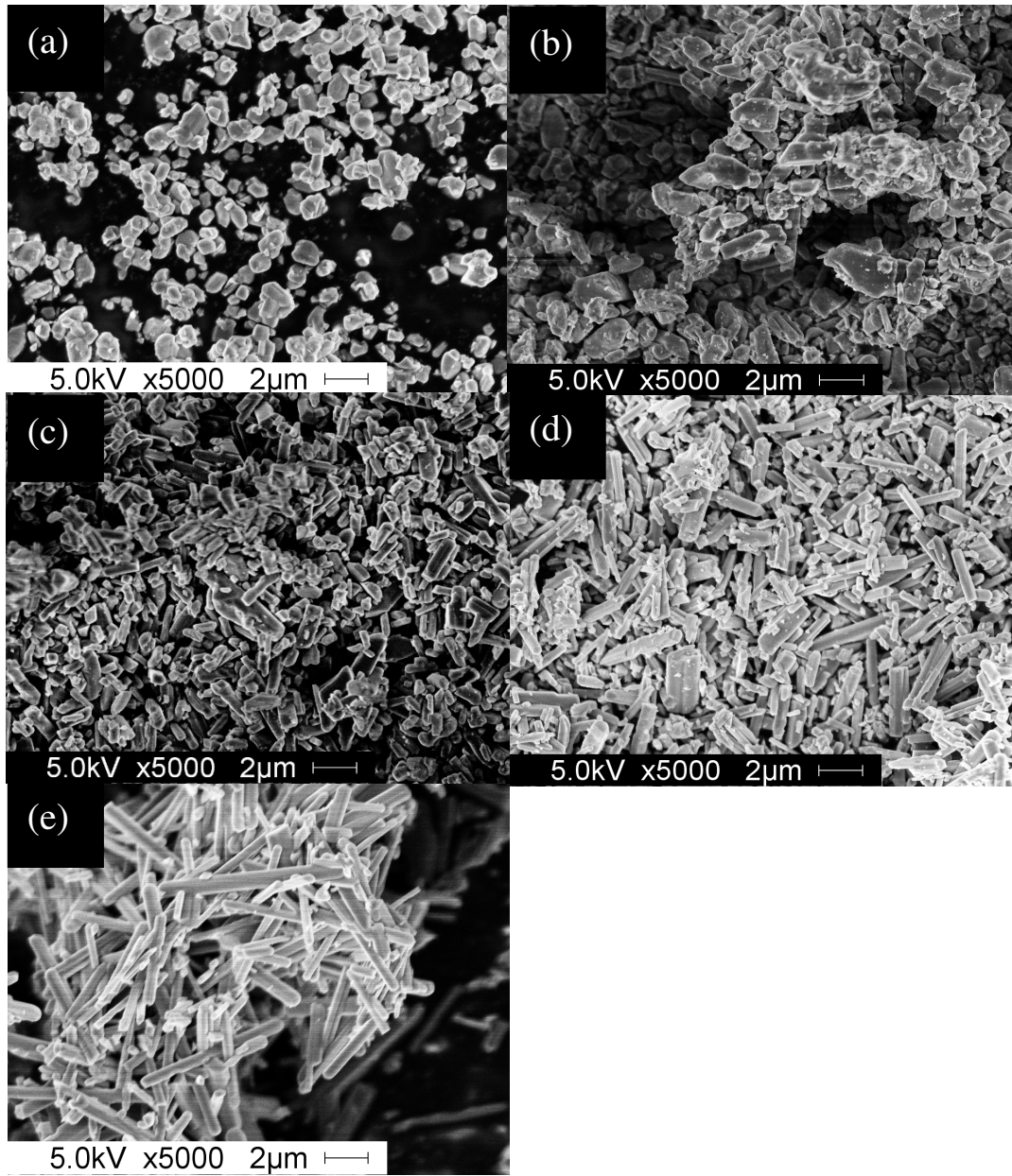


Fig. 2. SEM images of various Rh/KTO(x ,1373) samples, where x was the solute concentration in mol.%, (a) Rh/KTO(SSR,100,1373), (b) Rh/KTO(90,1373), (c) Rh/KTO(50,1373), (d) Rh/KTO(30,1373), and (e) Rh/KTO(10,1373).

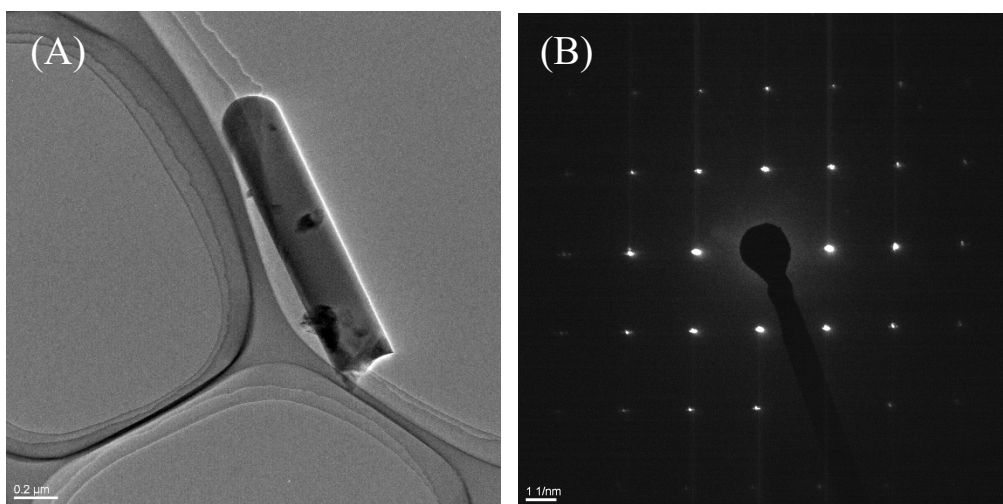


Fig. 3. (A) TEM image and (B) electron diffraction pattern of the Rh/KTO(10,1373) sample.

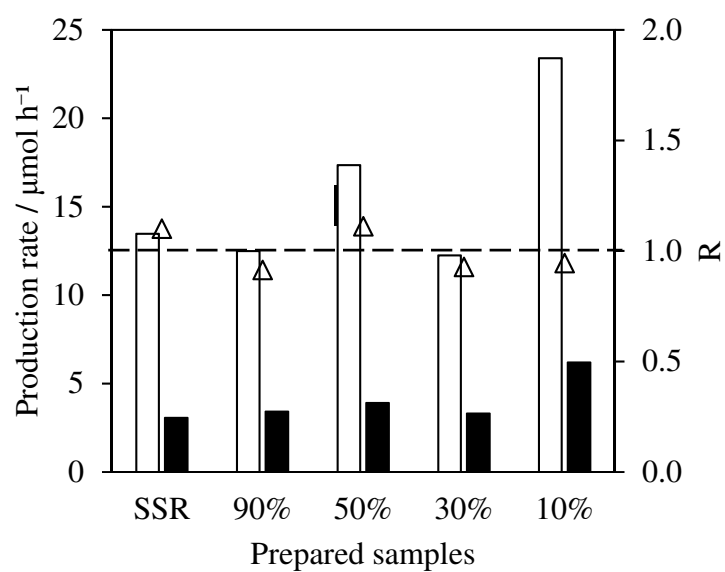


Fig. 4. Production rates of H₂ (white bar) and CO₂ (black bar) in the photocatalytic reaction test for the PSRM reaction, and the consumed electron/hole ratio calculated from the production rates, $R(e^-/h^+)$ (open triangle), over the Rh/KTO(*x*,1373) samples. The reaction conditions are the same as those mentioned in the caption of Fig. 1.

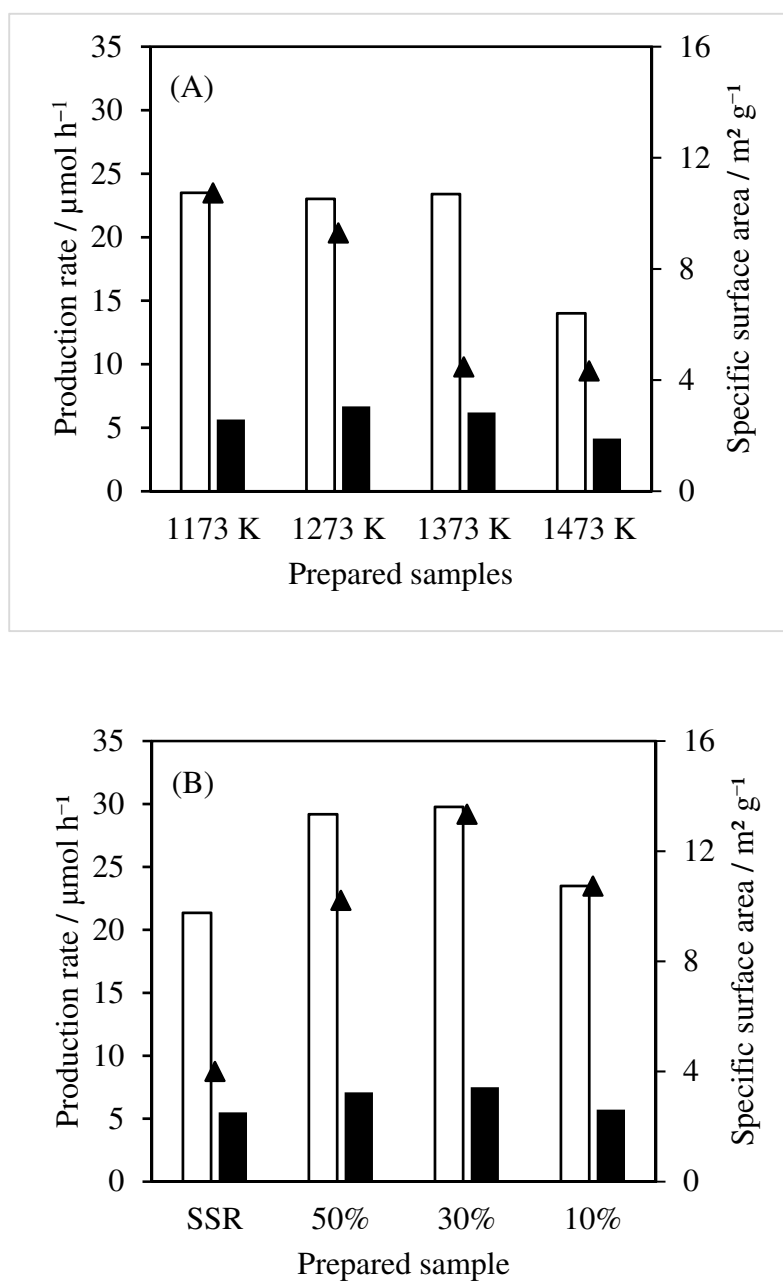


Fig. 5. Production rates of H_2 (white bar) and CO_2 (black bar), and the specific surface area (filled triangle) of (A) various Rh/KTO(10,y) samples and (B) various Rh/KTO(x,1173) samples. The reaction conditions are the same as those mentioned in the caption of Fig. 1.

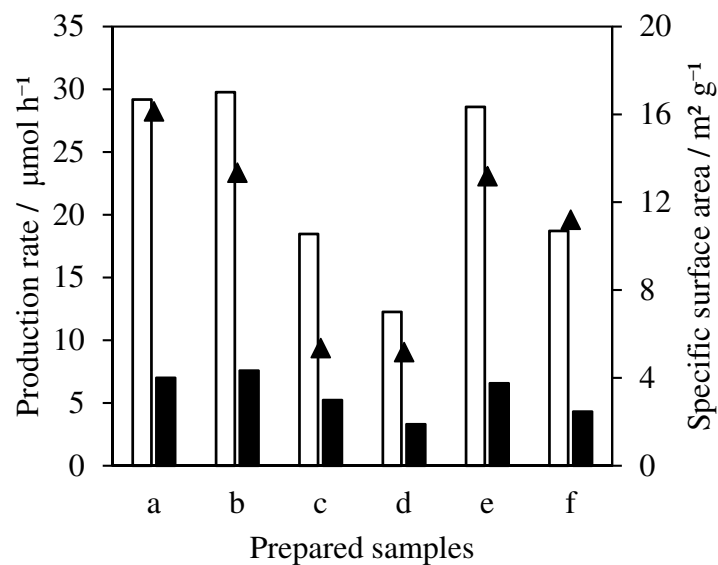


Fig. 6. Production rates of H_2 (white bar) and CO_2 (black bar), and the specific surface area (filled triangle) of the Rh/KTO(30,y) samples, (a) Rh/KTO(30,1073), (b) Rh/KTO(30,1173), (c) Rh/KTO(30,1273), (d) Rh/KTO(30,1373), (e) Rh/KTO(30,1173)1h, and (f) Rh/KTO(30,1173)ana. The reaction conditions are the same as those mentioned in the caption of Fig. 1.

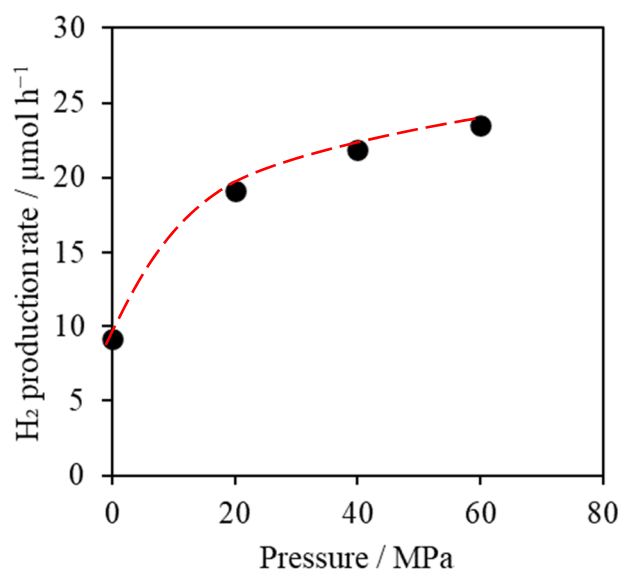


Fig. 7. H_2 production rate of the powder (0 MPa) and granule (20-40 MPa) Rh/KTO(10,1373) samples, where the catalyst weights were 0.34, 0.45, 0.62, and 0.67

g, respectively to regulate the photoirradiation area as 6 cm^2 . The reactant gas mixture (25% CH_4 , 2.4% H_2O , and 72.6% Ar) was introduced at the flow rate of 15 ml min^{-1} . The light intensity used was 165 mW cm^{-2} when measured at $254 \pm 10\text{ nm}$ in wavelength. Products were sampled at 3 hours later after starting photoirradiation

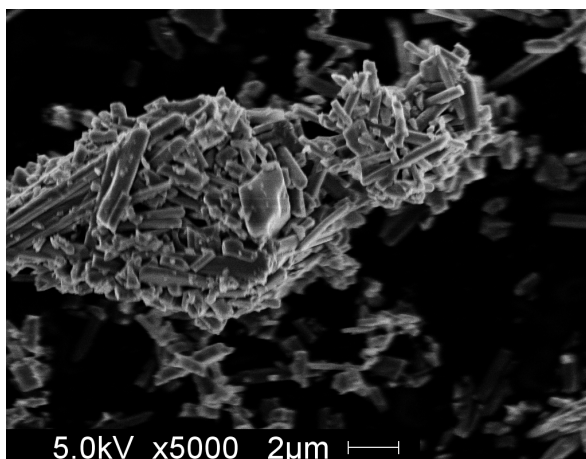


Fig. 8. SEM images of the granule Rh/KTO(10,1373) sample.

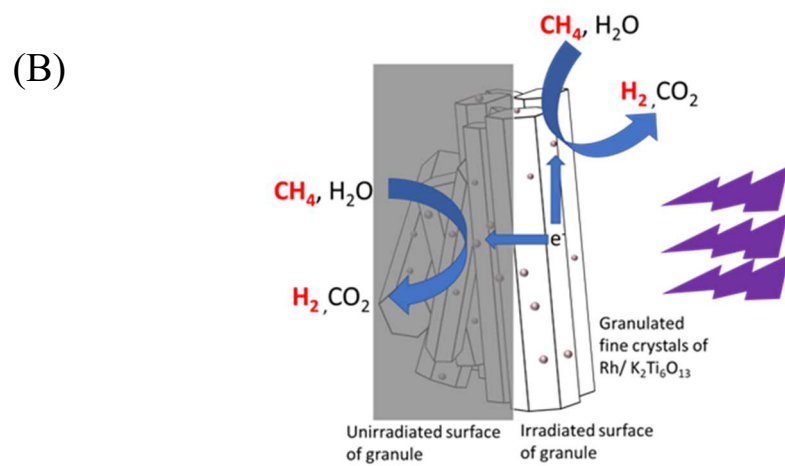
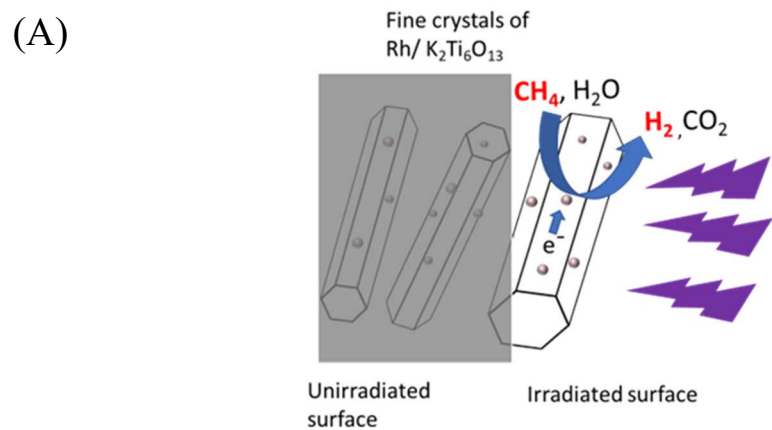


Fig. 9. Illustrations of the Rh/KTO samples consisting of (a) the powdery fine crystals, and (b) the granulated fine crystals for the PSRM.