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A highly active photocatalyst for overall water splitting with a hydrated layered perovskite structure

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Abstract

Photocatalytic decomposition of H_2O into H_2 and O_2 over a novel photocatalyst, $K_2La_2Ti_3O_{10}$, was accomplished. $K_2La_2Ti_3O_{10}$, a layered perovskite-type compound with a hydrated interlayer space, exhibited a high activity for overall water splitting with Ni-loading. The highest activity was obtained over Ni(3.0 wt%)–$K_2La_2Ti_3O_{10}$ when the reaction was carried out in aqueous KOH solution (0.1 M, pH = 12.8). By comparison with other Ni-loaded photocatalysts reported previously, the reaction mechanism of Ni–$K_2La_2Ti_3O_{10}$ was discussed. © 1997 Elsevier Science S.A.

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1. Introduction

We have reported that some layered compounds which can intercalate reactants into the interlayer space exhibit high photocatalytic activity [1–5]. $K_4Nb_6O_{17}$, an ion-exchangeable layered compound, was first found to show high photocatalytic activity for overall water splitting. $K_4Nb_6O_{17}$ is hydrated during the reaction, and photoexcited electrons and holes can react at the interlayer space without migrating to the external surface of the particle (1–10 μm) [1,6].

The family of layered perovskite-type compounds generally formulated as $A'[A_2B_3O_{10}]$ (A' = K, Rb, Cs; A = La, Ca, Pb; B = Nb, Ti, etc.) was also found to show interesting photocatalytic behavior [3–5]. For example, $KCa_2Nb_3O_{10}$ and $KSr_2Nb_3O_{10}$ are not hydrated, but these compounds become hydrated by replacing K^+ ions with H^+ ions in a concentrated acidic solution. In the case of H^+-exchanged forms, the interlayer space is available as a reaction site and photocatalytic activity for H_2 evolution from aqueous MeOH solution is markedly enhanced [4]. More significantly, the layered perovskite-type family has a lot of derivatives by replacing elements of the layer with other elements and some of them, such as $RbPb_2Nb_3O_{10}$ [3], show some photoresponse under visible light irradiation.

However, overall water splitting has never been accomplished over these layered perovskite-type compounds although these H^+-exchanged forms exhibit high activities in the presence of so-called ‘‘sacrificial reagents’’ such as MeOH [4]. In general, to accomplish overall water splitting, the reaction is carried out in an alkaline solution [1,2,7,8]. These H^+-exchanged forms are not hydrated in an alkaline solution due to the reverse ion exchange reaction resulting in the K^+-exchanged form, and consequently the interlayer space is not available.

On the other hand, $K_2La_2Ti_3O_{10}$, which is also a layered perovskite-type compound, is hydrated even in the original form [9], and was found to exhibit high activity for overall water splitting by Ni-loading. The structure of $K_2La_2Ti_3O_{10}$ is illustrated schematically in Fig. 1. $K_2La_2Ti_3O_{10}$ consists of negatively charged titanolanthanate perovskite layers and interlayer K^+ ions. This is the second example of overall water splitting following $A_4Nb_6O_{17}$ (A = K,Rb) catalysts among layered compounds [1,2]. In this paper, we have examined the photocatalytic activity and properties of $K_2La_2Ti_3O_{10}$, and discussed the reaction mechanism of Ni–$K_2La_2Ti_3O_{10}$ by comparison with other Ni-loaded photocatalysts reported previously [1,6,7,10].

2. Experimental

$K_2La_2Ti_3O_{10}$ was prepared from K_2CO_3, La_2O_3 and TiO_2 powders. These stoichiometric mixtures were first calcined at 1173 K for 5 h followed by grinding and recalcination at 1323 K for 40 h.

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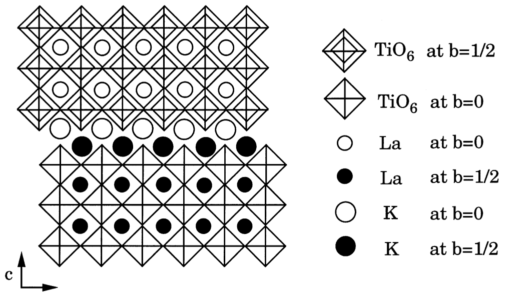
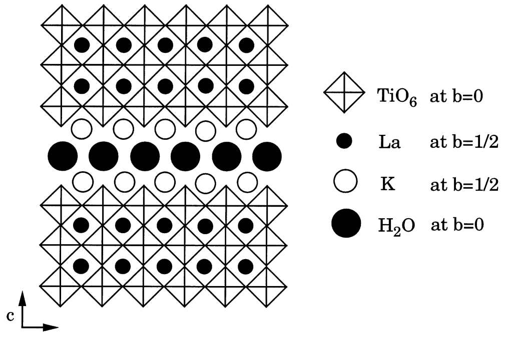


(a) $K_2La_2Ti_3O_{10}$



(b) $K_2La_2Ti_3O_{10} \cdot H_2O$

Fig. 1. Schematic structures of (a) $K_2La_2Ti_3O_{10}$ and (b) $K_2La_2Ti_3O_{10} \cdot H_2O$.

The procedures for Ni-loading and activating pretreatment were carried out by previously described methods [1,2,7,8]. After adding the required amount of aqueous $Ni(NO_3)_2$ solution, the sample was dried by heating on a water bath followed by calcination in air for about 20 min. Then the catalyst was activated as follows; the catalyst was reduced by H_2 at 773 K for 2 h followed by O_2 oxidation for 1 h at 473 K in a closed gas circulation system. By this pretreatment, only the outer side of the Ni particles is reoxidized [6,7,10]. Thus the catalyst loaded with Ni should be described precisely as NiO_x–$K_2La_2Ti_3O_{10}$ $(0<x<1)$, but is referred to as Ni–$K_2La_2Ti_3O_{10}$ in this paper.

Photocatalytic reactions were carried out in a closed gas circulation system. The catalyst (1 g) was dispersed in distilled water (320 ml) containing KOH by magnetic stirring and irradiated by a high-pressure mercury lamp (450 W) equipped with an inner irradiation-type quartz cell in the presence of gaseous Ar at 50 torr. The evolved gases were analyzed with gas chromatography (TCD, Ar carrier) with a molecular sieve 5A column, which was attached directly to the closed gas circulation system.

The catalyst was characterized by X-ray diffraction (XRD) and ultraviolet–visible diffuse reflectance spectroscopy (UV-DRS).

3. Results and discussion

3.1. Characterization

In Fig. 2, the XRD patterns of $K_2La_2Ti_3O_{10}$ under dry and wet conditions are shown. The dry and wet samples were the catalyst powder calcined (dry) and that filtered after suspension in distilled water for 5 h (wet), respectively. Under wet conditions, the d(001) diffraction peak shifted to a lower angle compared with that under dry conditions, which indicates the expansion of the *c*-axis length from 14.9 to 16.9 Å. It is known that $K_2La_2Ti_3O_{10}$ with *c*-axis length of 14.9 Å is not hydrated and possesses the structure as illustrated in Fig. 1(a) and that $K_2La_2Ti_3O_{10}$ with *c*-axis length of 16.9 Å is in the form of $K_2La_2Ti_3O_{10} \cdot H_2O$ with a hydrated interlayer space as illustrated in Fig. 1(b) [9]. $K_2La_2Ti_3O_{10}$ is thus easily hydrated in an aqueous solution as well as in highly humid air. Therefore, in some cases, the catalyst should be precisely described as $K_2La_2Ti_3O_{10} \cdot H_2O$, but it is simply referred to as $K_2La_2Ti_3O_{10}$ in this paper.

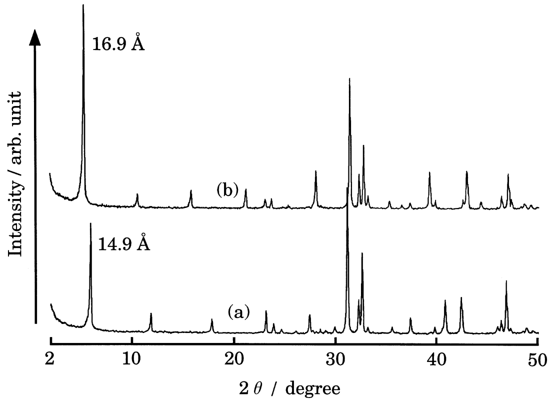


Fig. 2. X-ray diffraction patterns of $K_2La_2Ti_3O_{10}$ under (a) dry and (b) wet conditions.

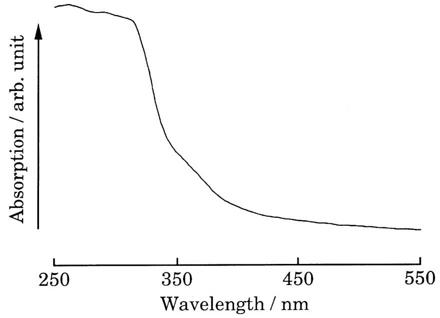


Fig. 3. UV-diffuse reflectance spectrum of $K_2La_2Ti_3O_{10}$.

Fig. 3 shows the UV-diffuse reflectance spectrum of $K_2La_2Ti_3O_{10}$ powder. Some absorption tail at around 350 nm was observed in the spectrum of $K_2La_2Ti_3O_{10}$. It was probably the absorption of some impurity. $K_2La_2Ti_3O_{10}$ had an absorption band in the ultraviolet region, and the band gap of this compound was estimated to be about 3.5 eV from the absorption edge.

3.2. Photocatalytic activity of $K_2La_2Ti_3O_{10}$

In general, the activity of overall water splitting is considerably dependent on the condition of the solution, and it is known that overall water splitting efficiently proceeds in an alkaline solution [1,2,7,8]. Here, we examined the dependence of the activity on the concentration of aqueous KOH solution and on the amount of loaded Ni. Fig. 4 shows the time course of H_2 and O_2 evolution under the optimum conditions. The highest activity was obtained over 3.0 wt% of Ni-loaded $K_2La_2Ti_3O_{10}$ and the reaction was carried out in 0.1 M aqueous KOH solution where the pH was about 12.8. More than 400 μmol h^{-1} of H_2 evolution was observed and the reaction proceeded steadily with an almost stoichiometric ratio of H_2 and O_2. This value corresponds to 60% of that of the Ni(0.1 wt%)-$K_4Nb_6O_{17}$ catalyst obtained under the same condition. As for the bulk-type photocatalyst, simultaneous evolution of H_2 and O_2 is rarely observed. Therefore, it is considered that the high activity of the Ni–$K_2La_2Ti_3O_{10}$ catalyst was derived from use of the interlayer space as a reaction site. The slight shortage of O_2 evolved, less than the stoichiometric ratio, is often observed in water splitting for reasons such as the presence of impurities, partially reduced semiconductors or oxidized species of water trapped in the catalyst. The amount of H_2 and O_2 evolved increased in proportion to the irradiation time. This means that photocatalytic water splitting on $K_2La_2Ti_3O_{10}$ is a zero-order reaction and that the reverse reaction from evolved H_2 and O_2 into H_2O is almost negligible. The outer side of the Ni particles become NiO by the pretreatment of reoxidation at 473 K for 1 h, which makes it possible to prevent the loss of products for the reverse reaction from H_2 and O_2 into H_2O [6,7,10]. The Ni–$K_2La_2Ti_3O_{10}$ catalyst without the pretreatment of reoxidation was used for water splitting, the rates of gas evolution decreased with time as shown in Fig. 5.

The dependence of the activity of photocatalytic decomposition of water on the amount of loaded Ni is shown in Fig. 6. H_2 and O_2 were evolved simultaneously even over $K_2La_2Ti_3O_{10}$ alone, although the rate of O_2 evolution was less than the stoichiometric amount. The activities, especially O_2 evolution, were markedly enhanced by Ni-loading. Although the rate of O_2 evolution was more enhanced than that of H_2 evolution by Ni-loading, it does not necessarily mean that loaded Ni works as the site for O_2 evolution. In general, Ni accelerates the H_2-formation rate [1,7]. As H_2 is evolved predominantly, the number of photoexcited holes existing in a $K_2La_2Ti_3O_{10}$ particle becomes larger than that of electrons, which leads to an increase in the rate of O_2 evolution. Photogenerated charges were thus separated. The activity of O_2 evolution was simply enhanced up to the stoichiometric ratio. When the catalyst was loaded with 3.0 wt% of Ni, the activity reached a maximum, and further Ni-loading led to saturation of activity. The color of the Ni-loaded photocatalyst changed from gray to black at around 2.0–3.0 wt% of Ni-loading. The number of photons absorbed into the $K_2La_2Ti_3O_{10}$ particles became attenuated at large amounts of Ni-loading, which was probably the cause of the saturation of activity. A larger amount of loaded Ni was required for $K_2La_2Ti_3O_{10}$ to obtain the highest activity compared with other Ni-loaded photocatalysts reported previously [1,2,8,10].

In Fig. 7, the dependence of the activity of the photocatalytic decomposition of water on the concentration of aqueous KOH solution is shown. The activity was enhanced by the addition of KOH up to 0.1 mol l^{-1} where the pH was about 12.8, but further addition of KOH led to the suppression of activity. Suppression of activity in a concentrated alkaline

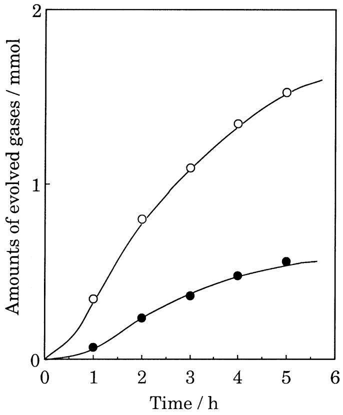


Fig. 5. Time course of gas evolution from aqueous KOH (0.1 M) solution over Ni(3.0 wt%)–$K_2La_2Ti_3O_{10}$ catalyst without reoxidation by O_2 at 473 K for 1 h: ○, H_2; ●, O_2; 1 g catalyst; 320 ml H_2O; high-pressure Hg lamp (450 W) light source; inner irradiation-type quartz reaction cell.

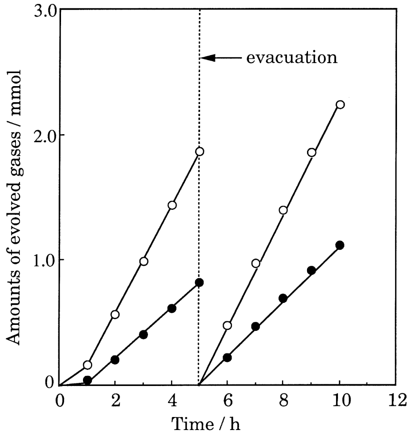


Fig. 4. Time course of gas evolution from aqueous KOH (0.1 M) solution over Ni(3.0 wt%)–$K_2La_2Ti_3O_{10}$ catalyst: ○, H_2; ●, O_2; 1 g catalyst; 320 ml H_2O; high-pressure Hg lamp (450 W) light source; inner irradiation-type quartz reaction cell.

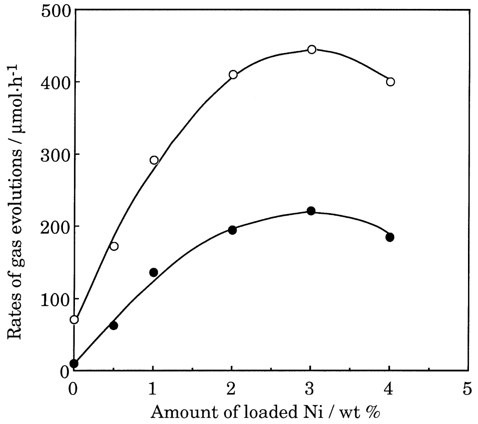


Fig. 6. Dependence of the activity of photocatalytic decomposition of water on the amount of loaded Ni: ○, H_2; ●, O_2; 1 g catalyst; 320 ml H_2O; high-pressure Hg lamp (450 W) light source; inner irradiation-type quartz reaction cell.

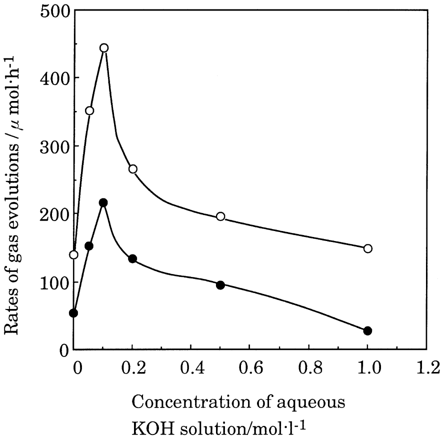


Fig. 7. Dependence of the activity of the photocatalytic decomposition of water on the concentration of aqueous KOH solution: ○, H_2; ●, O_2; 1 g catalyst; 320 ml H_2O; high-pressure Hg lamp (450 W) light source; inner irradiation-type quartz reaction cell.

Table 1
Photocatalytic activity of $K_2La_2Ti_3O_{10}$ with various modifications

Loaded metal or metal oxide	Solution	Rate of gas evolution/ μmol h^{-1}	
		H_2	O_2
Ni (3.0 wt%)	0.1 M KOH aq	444	221
Pt (0.1 wt%)	1.5 M Na_2CO_3 aq	trace	0
RuO_2 (1.0 wt%)	0.1 M KOH aq	52	0
RuO_2 (1.0 wt%)	1.5 M Na_2CO_3 aq	12	trace

Catalyst, 1 g; H_2O, 320 ml; light source, high-pressure Hg lamp (450 W); reaction cell, inner irradiation-type quartz cell.

solution was also observed over a Ni–$K_4Nb_6O_{17}$ catalyst [1]. Ni–$K_2La_2Ti_3O_{10}$ is easily degraded in a concentrated acidic solution but it is stable in a concentrated alkaline solution. Thus the suppression of activity in a concentrated KOH solution was not due to the degradation of the catalyst. It is considered that the decrease in the concentration of H^+ ions as reactants leads to the suppression of activity.

Several methods for the modification of $K_2La_2Ti_3O_{10}$ were attempted as summarized in Table 1. Loaded metals [11–14] have been reported to be effective for overall water splitting. As is clearly shown, only the Ni–$K_2La_2Ti_3O_{10}$ catalyst was able to accomplish overall water splitting. O_2 evolution was observed only in the initial stage of irradiation over RuO_2-loaded $K_2La_2Ti_3O_{10}$ suspended in a concentrated aqueous Na_2CO_3 solution.

3.3. *Comparison of Ni–$K_2La_2Ti_3O_{10}$ with other Ni-loaded photocatalysts*

We have previously reported some Ni-loaded photocatalysts for overall water splitting, including Ni–$SrTiO_3$ [7,10], a bulk-type photocatalyst, and Ni–$K_4Nb_6O_{17}$ [1,6], with a hydrated layered structure, both of which decomposed H_2O into H_2 and O_2. Here, Ni–$K_2La_2Ti_3O_{10}$ also decomposed H_2O into H_2 and O_2 at a stoichiometric ratio by using a similar manner of pretreatment. However, some remarkably different behavior was observed with the $K_2La_2Ti_3O_{10}$ catalyst compared with other Ni-loaded photocatalysts. The $K_2La_2Ti_3O_{10}$ catalyst exhibited the highest activity of Ni-loading by 3.0 wt%, while $K_4Nb_6O_{17}$ required only 0.1 wt% of Ni-loading to exhibit the highest activity [1]. What is the difference? $K_4Nb_6O_{17}$ possesses two kinds of interlayer space, interlayer I and II, which appear alternately. Our previous work showed that almost all the loaded Ni (0.1 wt%) was located only at the interlayer space I as ultrafine particles due to the different ion-exchangeability of interlayer I from that of II [6]. In such a morphology, Ni works efficiently as a H_2-forming site. The difference in their optimum amounts of Ni-loading was probably due to the difference in their morphology, which might also indicate the difference in their reaction mechanisms. in fact, $K_4Nb_6O_{17}$ possesses a peculiar reaction mechanism; Ni metal ultrafine particles as H_2-forming sites are located at the interlayer space I which is completely separated by a niobate sheets from the O_2-forming sites, i.e. interlayer space II [6]. Due to this separation of each reaction site derived from the peculiar structure of $K_4Nb_6O_{17}$, decomposition of H_2O into H_2 and O_2 is efficiently attained. However, such a scheme is not applicable to the $K_2La_2Ti_3O_{10}$ catalyst which has only one kind of interlayer space. From scanning electron microscope observations, most of the Ni particles are located on the external surface of the $K_2La_2Ti_3O_{10}$ particles, although a similar procedure to $K_4Nb_6O_{17}$ of Ni-loading was applied. Consequently, it is considered that the morphology of active Ni particles on $K_2La_2Ti_3O_{10}$ is similar to that of Ni–$SrTiO_3$, a bulk-type photocatalyst [7]. However, it does not immediately indicate that the photocatalytic reaction proceeds only on the external surface of the $K_2La_2Ti_3O_{10}$ particles, because the $K_2La_2Ti_3O_{10}$ catalysts exhibited higher activity than those of other bulk-type photocatalysts loaded with Ni [7,8,13]. The high activity of $K_2La_2Ti_3O_{10}$ was probably derived from utilization of the interlayer space as a reaction site. How is the interlayer space utilized for reaction? One of the possibilities to be inferred is that the interlayer space is used for O_2-forming sites. This is consistent with the general mobility of photoexcited electrons and holes; excited electrons have larger diffusion length compared with excited holes. Therefore, excited electrons may be able to migrate easily to the Ni particles located on the external surface of $K_2La_2Ti_3O_{10}$ particles, and excited holes with small diffusion length may react with H_2O at the interlayer space to form O_2. As for the bulk-type photocatalysts, the surface of the semiconductor particles exposed to the liquid H_2O was required to evolve O_2, and excessive Ni-loading decreased the O_2-formation sites. Assuming that O_2 was evolved on the external surface of the $K_2La_2Ti_3O_{10}$ particles, excessive Ni-loading should lead to decrease in activity. However, $K_2La_2Ti_3O_{10}$ required large amounts of Ni-loading to exhibit optimum activity. This may indicate that $K_2La_2Ti_3O_{10}$ does not require O_2-formation sites on the external surface of $K_2La_2Ti_3O_{10}$ particles on account of O_2 evolution at the interlayer space. In any events, further detailed study is necessary to understand the reaction mechanism.

In summary, overall water splitting was accomplished over a novel photocatalyst, $K_2La_2Ti_3O_{10}$, as a first example among layered perovskite-type compounds. The highest activity was obtained over Ni(3.0 wt%)–$K_2La_2Ti_3O_{10}$ when the reaction was carried out in aqueous KOH solution (0.1 M, pH 12.8). Much higher activity was obtained than that of other bulk-type photocatalysts.

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