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Preparation of $K_2La_2Ti_3O_{10}$ by Polymerized Complex Method and Photocatalytic Decomposition of Water

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A polymerized complex (PC) technique was applied to the preparation of a highly active photocatalyst, $K_2La_2Ti_3O_{10}$, with a layered perovskite type structure to decompose H_2O into H_2 and O_2. The catalyst prepared by the PC technique had a higher photocatalytic activity than that prepared by conventional solid-state reaction method.

Introduction

Photocatalytic decomposition of water using several oxide semiconductors has been studied for conversion of photon energy into chemical energy. Since a prototypic system based on a TiO_2 photoelectrode was discovered in 1972,[1] many photocatalytic systems using TiO_2- and $SrTiO_3$-based photocatalysts have been reported.[2−9] However, the quantum efficiencies in most cases have remained at a considerably low level (ca. ~1%). We have reported that the photocatalytic systems using some ion-exchangeable layered oxides have several advantages compared with so-called “bulk” type oxides such as TiO_2 and $SrTiO_3$.[10−21] Among them, $K_4Nb_6O_{17}$ photocatalyst with Ni loading (0.1 wt %) was first found as such a layered photocatalyst that could stoichiometrically decompose water into H_2 and O_2 under the bandgap irradiation (>3.3 eV)[11−13] and showed a quantum efficiency of about 7−9% at 300 nm.[11−13] The high efficiency was attributed to the usage of the interlayer space where intercalated water molecules were decomposed into H_2 and O_2.

Recently, an ion-exchangeable layered perovskite type oxide, $K_2La_2Ti_3O_{10}$ with Ni loading was also found to decompose water.[18,20] It was also spontaneously hydrated even under ambient condition.[22] While $K_4Nb_6O_{17}$ has two different types of interlayer spaces[23−25] and the loaded Ni exists at the interlayer space as ultrafine particles,[11−13] $K_2La_2Ti_3O_{10}$ has only one type of interlayer space and most of the loaded Ni exists at the external surface. Thus, the reaction mechanism of water decomposition on $Ni/K_2La_2Ti_3O_{10}$ was proposed as follows; H_2 evolves on Ni particles at the external surface and O_2 evolves at the interlayer space.[18,20] We also found that the fine particles prepared by ball-milling of the $K_4Nb_6O_{17}$ catalyst after recalcination at 773 K showed higher photocatalytic activity than the original one.[19] The effect of the particle size suggests that the interlayers at the inner part of large particles (~10 μm) are not so effectively utilized for decomposing water.[21] Therefore, preparation of fine particles with a good crystallinity is desirable for the improvement of the catalyst.

In general, these compounds are synthesized by the conventional ceramic route, in which appropriate

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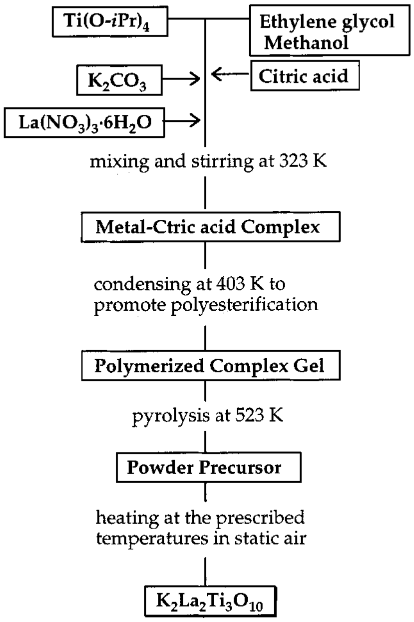

Figure 1. Flowchart for preparing $K_2La_2Ti_3O_{10}$ by the PC method.

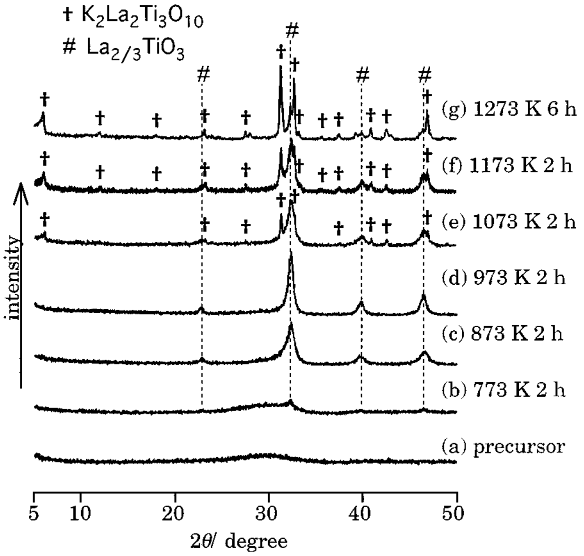

Figure 2. XRD patterns of the stoichiometric precursor (K/La/Ti = 2/2/3) (a) and that heated in air at 773 K for 2 h (b), at 873 K for 2 h (c), at 973 K 2 h (d), at 1073 K 2 h (e), at 1173 K 2 h (f) and at 1273 K 6 h (g). # and † denote diffractions from $La_{2/3}TiO_3$ and $K_2La_2Ti_3O_{10}$, respectively.

amounts of metal oxides or carbonates are mixed, and then the mixture is heated for a long period at high temperatures to allow interdiffusion of the cations. One of the serious problems of this method is the great difficulty in preparing the compounds in their pure form at relatively low temperatures. The attempts to synthesize these layered compounds by utilizing sol–gel techniques that require shorter heating time at relatively low temperatures are expected to enable us to produce layered photocatalysts with small particle size (high surface area).

The polymerized complex (PC) method, a gel technique, is known as the Pechini method.[26] The method is based on polymerization between ethylene glycol (EG) and citric acid (CA) in the presence of soluble metal–CA complexes; the complexes are immobilized in a rigid polyester network almost in the molecular level as in the original solution.[27–34] Immobilization of the metal complexes can inhibit hydroxylation of the individual metal cations, that might occur in the alkoxide-based sol–gel techniques.

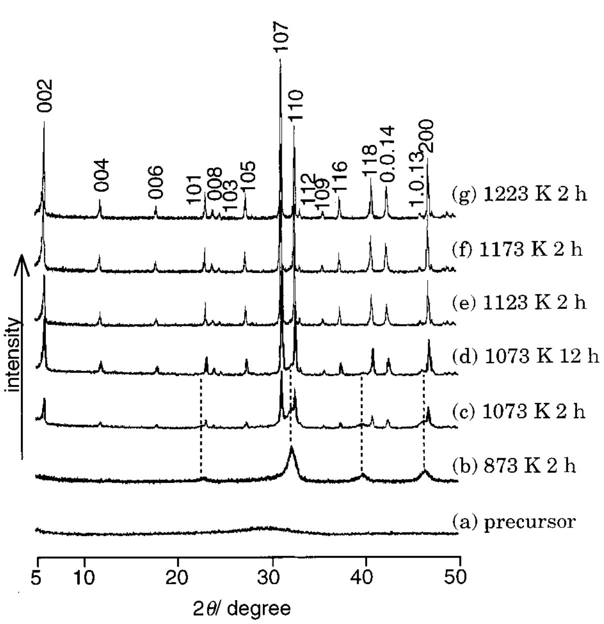

Figure 3. XRD patterns of the precursor containing 100% excess of potassium (K/La/Ti = 4/2/3) (a) and that heated in the air at 873 K for 2 h (b), at 1073 K for 2 h (c), at 1073 K for 12 h (d), at 1123 K for 2 h (e), at 1173 K for 2 h (f), and at 1223 K for 2 h (g).

In the present work, we report a synthesis of a layered perovskite type oxide, $K_2La_2Ti_3O_{10}$, using the PC method, and the photocatalytic activity of water splitting on the catalyst are compared with that prepared by the conventional solid-state reaction method.

Experimental Section

Preparation of $K_2La_2Ti_3O_{10}$ Powders. The $K_2La_2Ti_3O_{10}$ powders were synthesized by the PC method as outlined in Figure 1. $Ti[OCH(CH_3)_2]_4$ (Ti(O*i*Pr)$_4$), $La(NO_3)_3\cdot 6H_2O$, and K_2CO_3 were selected as starting materials. The following description is for the preparation of about 5 g of $K_2La_2Ti_3O_{10}$. Ethylene glycol (EG) and methanol (MeOH) were used as solvents, and anhydrous citric acid (CA) was used as a complexing agent to stabilize Ti, La, and K ions against water generated during the polymerization between EG and CA. Ti(O*i*Pr)$_4$ (5.68 g, 20 mmol) was first dissolved in the mixture of MeOH (51 g, 1.6 mol) and EG (50 g, 0.8 mol), and CA (38 g, 0.2 mol) was subsequently added with continuous stirring in order to convert Ti(O*i*Pr)$_4$ to stable Ti–CA complexes. After

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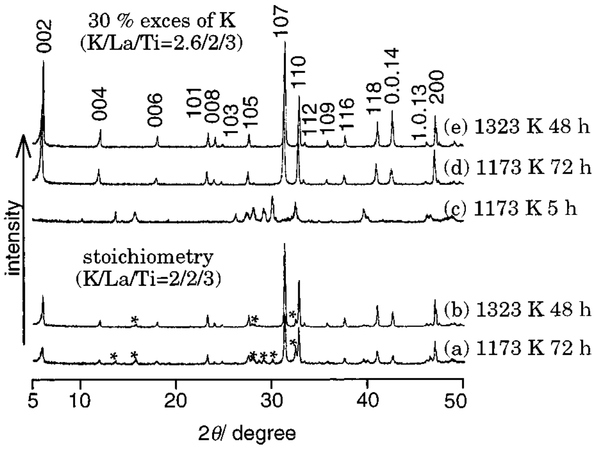

Figure 4. XRD patterns of the products obtained by heating the stoichiometric mixture of K_2CO_3, La_2O_3, and TiO_2 (K/La/Ti = 2/2/3) in air at 1173 K for 72 h (a) and at 1323 K for 48 h (b) and by heating the mixture containing 30% excess of potassium (K/La/Ti = 2.6/2/3) in air at 1173 K for 5 h (c), at 1173 K for 72 h (d), and at 1323 K for 48 h (e). * denotes the diffraction from other impurity phases.

Table 1. EDX Measurements of the Ratio of K, La, and Ti Atoms Containing the Obtained Products by the PC Method and That of Theoretical Value (atom %)

	stoichiometric precursor		excess potassium (100%) precursor	
element	calcination at 873 K for 2 h	calcination at 1173 K for 2 h	calcination at 1173 K for 2 h	theoretical values
K (K)	27	15	30	28.6
La (L)	32	39	28	28.6
Ti (K)	41	46	42	42.8

complete dissolution was achieved, K_2CO_3 was added. The amount of K_2CO_3 was controlled between stoichiometry (0.92 g, 13.3 mmol) and twice excess (1.84 g, 26.7 mmol) in order to compensate for the loss of potassium by volatilization. (Preparation conditions in controlling amount of potassium were discussed in the later section; see Figures 2 and 3.) The mixture was stirred at room temperature until it became transparent. Then, $La(NO_3)_3{\cdot}6H_2O$ (5.77 g, 13.3 mmol) was added, and the solution was stirred at 323 K for a few minutes. The transparent solution thus obtained was heated at 403 K with continuous stirring to accelerate polymerization, and excess solvents (MeOH and H_2O) were removed. After the continuous heating at 403 K for several hours, the solution became highly viscous, and it finally gelled into a transparent brown resin. There was no formation of visible precipitation during the polymerization; the mixture of K, La, and Ti cations was considered to remain as molecularly homogeneous. Calcining the resin in an electric furnace at 673 K for a few hours, it became a black powder, being referred to as a “precursor” hereafter. The precursor was calcined at temperatures between 773 and 1273 K on an Al_2O_3 plate in air.

$K_2La_2Ti_3O_{10}$ was also prepared by the conventional solid-state reaction to compare with that prepared by the PC method. K_2CO_3, La_2O_3, and TiO_2 were mixed by mechanical grinding in a mortar. The composition of the mixtures was varied by two different amounts of K_2CO_3: the stoichiometric one and the other containing 30% excess of potassium. The mixture was calcined at 1173 K for 72 h at interval grindings for several times or 1323 K for 48 h.

Preparation of Active Ni/$K_2La_2Ti_3O_{10}$ Photocatalyst. $K_2La_2Ti_3O_{10}$ evolves H_2 and O_2 without Ni but the activity is markedly enhanced by Ni loading.[18,20] The detailed investigation was described elsewhere, and the preparation of an active Ni/$K_2La_2Ti_3O_{10}$ photocatalyst was carried out according to the literature.[8,13] Briefly, Ni was loaded by impregnation of $K_2La_2Ti_3O_{10}$ powder with an aqueous $Ni(NO_3)_2$ solution (3 atom % of Ni) followed by heating in the air at ca. 573 K for 20 min. The Ni-loaded catalyst was activated by H_2 reduction at 773 K for 2 h and subsequent reoxidation by O_2 at 473 K for 1 h.

Table 2. Dependence of Photocatalytic Activity and BET Surface Area of Ni−$K_2La_2Ti_3O_{10}$ (PC) upon Calcination Temperatures

calcination temp (K)[a]	rate of gas evolution (μmol·h^{-1}) H_2	rate of gas evolution (μmol·h^{-1}) O_2	BET surface area (m·g^{-1})
1073[b]	528	264	54
1123	1316	537	22
1173	2186	1131	5
1223	1042	427	3

[a] Calcination for 2 h. [b] For 12 h.

Characterization. The prepared catalysts were characterized by X-ray powder diffraction (XRD, Rigaku Geigerflex RAD-B, Cu Kα), energy-diffuse X-ray analysis (EDX, Akasi ISI DS130S), scanning electron microscopy (SEM, Akashi ISI DS130S), and UV−visible diffuse reflectance spectra (UV−vis DR spectra, Shimazu UV-240, ISR-240A).

Photocatalytic reaction was carried out in an air-free closed gas circulation system with an inner irradiation cell made of quartz (250 cm^3). The catalyst (1 g) was dispersed in an aqueous KOH solution (0.1 M, 300 cm^3) by magnetic stirring and was irradiated under Ar atmosphere (about 13.3 kPa) by a high-pressure Hg lamp (450 W). Amounts of evolved gases were analyzed by a gas chromatography (MS-5A column, Ar carrier) through a gas sampler (3 cm^3) which was directly connected to the reaction system to avoid any contamination from air.[8]

Results and Discussion

$K_2La_2Ti_3O_{10}$ Prepared by the PC Method. It is known that the addition of an excess of potassium is necessary for the synthesis of $K_2La_2Ti_3O_{10}$ in the pure form by the conventional solid-state reaction method, for compensation of the deficient amount of volatilized potassium.[22] A similar result has been observed in the present PC synthesis. Figure 2 shows XRD patterns of the precursor (derived from K/La/Ti = 2/2/3) and that calcined in air at various temperatures. The obtained precursor was amorphous in structure, as shown in Figure 2a. The products obtained at temperatures between 773 and 973 K for 2 h (Figure 7b−d) were assigned to the deficient perovskite of $La_{2/3}TiO_3$ (dashed lines). The desired $K_2La_2Ti_3O_{10}$ phase evolved at temperatures between 1073 and 1173 K for 2 h (Figure 2e,f, respectively) but $La_{2/3}TiO_3$ still remained as a main phase. Pure $K_2La_2Ti_3O_{10}$ phase could not be obtained even after heating the precursor at 1273 K for 6 h (Figure 2g). The formation of the deficient perovskite, $La_{2/3}TiO_3$, indicates that a part of potassium was lost due to volatilization.

The addition of an over stoichiometric amount of potassium to the “K/La/Ti CA/EG” solution was thus performed to compensate for the deficient amount of potassium. Figure 3 shows XRD patterns of the K/La/Ti = 4/2/3 composition precursor (containing 100% excess of potassium) and that calcined in air at temperatures between 873 and 1223 K. $La_{2/3}TiO_3$ phase primarily evolved at 873 K (Figure 3b) similarly to the product derived from the stoichiometric precursor (as shown in Figure 2c). $K_2La_2Ti_3O_{10}$ formed as a main phase at 1073 K for 2 h accompanied with the decrease of $La_{2/3}TiO_3$ phase (Figure 3c). As shown in diffraction patterns in Figure 3d−g, pure $K_2La_2Ti_3O_{10}$ could be obtained by calcination at 1073 K for 12 h or at higher

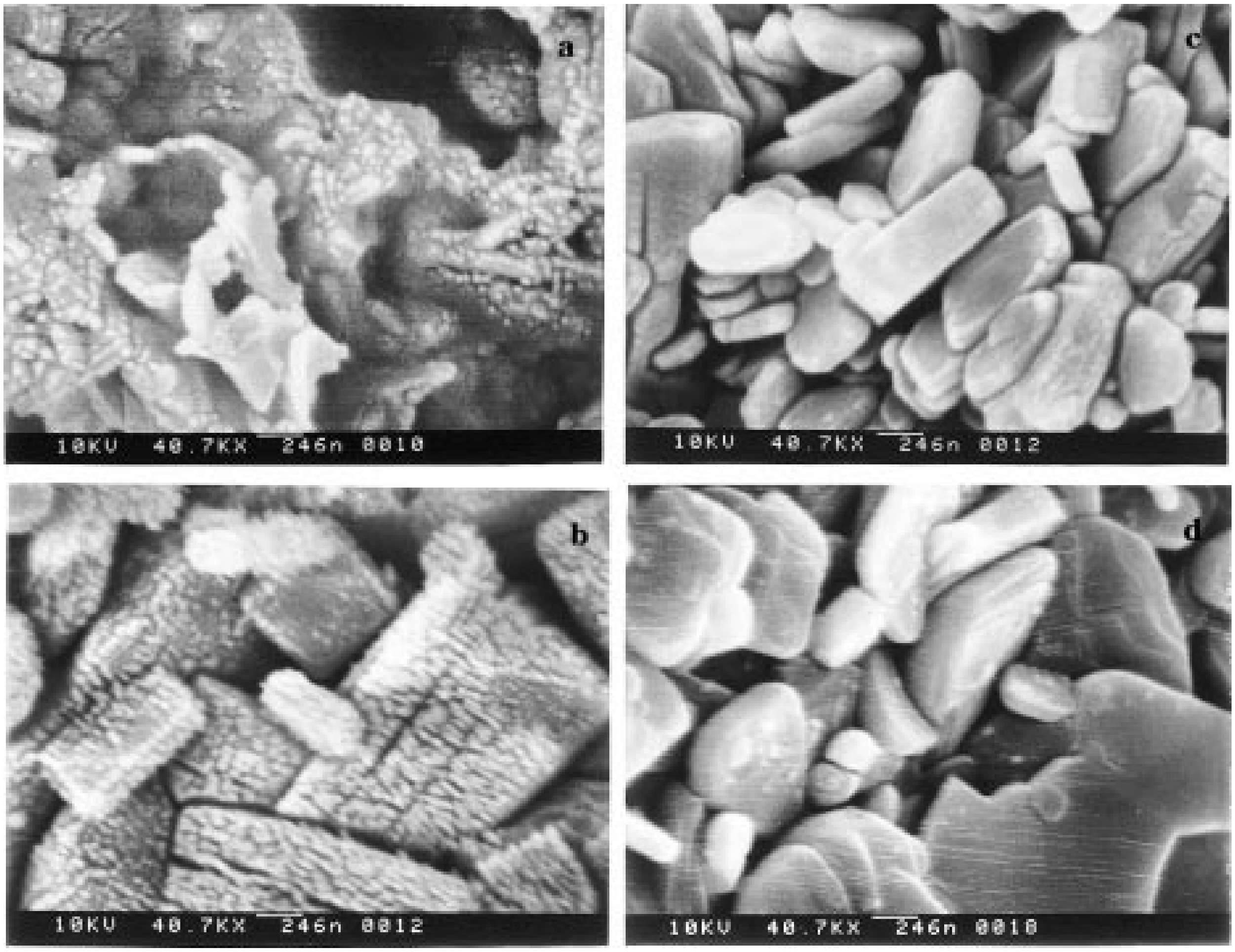

Figure 5. SEM photographs of $K_2La_2Ti_3O_{10}$ prepared by the PC method at 1073 K for 12 h (a), at 1123 K for 2 h (b), at 1173 K for 2 h (c), and at 1223 K for 2 h (d).

temperatures between 1123 and 1223 K for 2 h. Table 1 summarizes EDX results of K/La/Ti ratios of the products obtained from the stoichiometric (K/La/Ti = 2/2/3) precursor calcined at 873 and 1173 K for 2 h and that obtained by calcination of the precursor containing 100% excess of potassium (K/La/Ti = 4/2/3) at 1173 K for 2 h. K/La/Ti ratio of the stoichiometric precursor heated at 873 K for 2 h almost corresponds to the theoretical value. However, the amount of potassium decreases to less than the theoretical value after calcination at 1173 K for 2 h. On the other hand, K/La/Ti ratio of the product obtained by heating the K/La/Ti = 4/2/3 precursor at 1173 K for 2 h is in good agreement with the theoretical value. As shown in the XRD results in Figures 2 and 3, the $La_{2/3}TiO_3$ phase primarily formed at relatively low temperatures (773–973 K) despite the existence of potassium in the precursors. Taking account of the EDX results, it is clear that potassium is not volatilized but cannot react with Ti or La at around 873 K; on the other hand, potassium can react with Ti or La but simultaneously volatilized at the high-temperature region (≥1073 K). Consequently, $La_{2/3}TiO_3$ remained when the stoichiometric precursor (K/La/Ti = 2/2/3) was used as the starting composite. For estimation of the appropriate amount of excess potassium, we carried out producing $K_2La_2Ti_3O_{10}$ by changing the amount of potassium (30%, 50%, and 5 times excess than stoichiometry). After each precursor was calcined at 1173 K for 2 h, pure $K_2La_2Ti_3O_{10}$ was also obtained from the precursors containing 30% or 50% excess of potassium, but another phase, $K_2Ti_2O_5$, was contained in the case of 5 times excess potassium content. There-

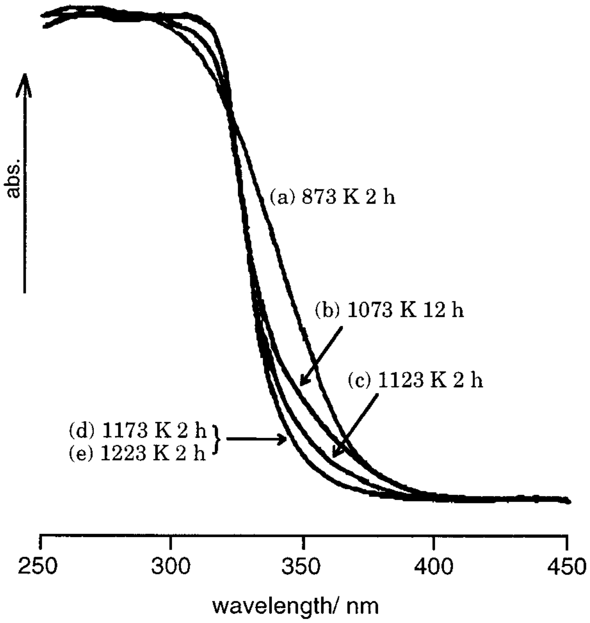

Figure 6. UV–vis DR spectra of the powders prepared by the PC method at 873 K for 2 h (a), at 1073 K for 12 h (b), at 1123 K for 2h (c), at 1173 K for 2 h (d), and at 1223 K for 2 h (e).

Table 3. Photocatalytic Activities of Ni−$K_2La_2Ti_3O_{10}$ Prepared by the Conventional Solid-State Reaction

preparation method	rate of gas evolution (μmol·h^{-1}) H_2	O_2	BET surface area (m^2·g^{-1})
30% excess of K[a] at 1173 K for 72 h	1255	632	4
30% excess of K[a] at 1323 K for 48 h	583	270	1
stoichiometric[b] at 1323 K for 48 h	444	220	1

[a] Prepared from the mixture containing 30% excess of K (K/La/Ti = 2.6/2/3). [b] Prepared from the stoichiometric mixture (K/La/Ti = 2/2/3).

fore, it is necessary for preparation of pure $K_2La_2Ti_3O_{10}$ by the PC method to add controlled excess amount of potassium to the precursor.

$K_2La_2Ti_3O_{10}$ Prepared by the Solid-State Reaction Method. To clarify the condition to prepare pure $K_2La_2Ti_3O_{10}$ by the conventional solid-state reaction route, two kinds of mixtures were compared: the one was stoichiometric composition, and the other contained 30% of excess potassium (K/La/Ti = 2.6/2/3). Both of them were calcined at 1173 or 1323 K. From the results of XRD measurement (shown in Figure 4), the products synthesized from the stoichiometric mixture (Figure 4a, calcined at 1173 K for 72 h; Figure 4b, calcined at 1323 K for 48 h) contain some impurity phases. On the contrary, pure $K_2La_2Ti_3O_{10}$ phase was formed by calcination of the mixture containing 30% excess of potassium at 1173 K for 72 h (Figure 4d) and at 1323 K for 48 h (Figure 4e). Additionally, pure $K_2La_2Ti_3O_{10}$ phase was also produced when the mixture of more excess of potassium (100%, K/La/Ti = 4/2/3) was used as a starting composite.

Comparing the product prepared at the same temperature by the PC method (Figure 3c, at 1173 K for 2 h) and the solid-state reaction method (Figure 4c, at 1173 K for 5 h), the former crystallized well but the latter did not. This indicates that the PC method has a considerably higher crystallization rate than the conventional solid-state reaction method.

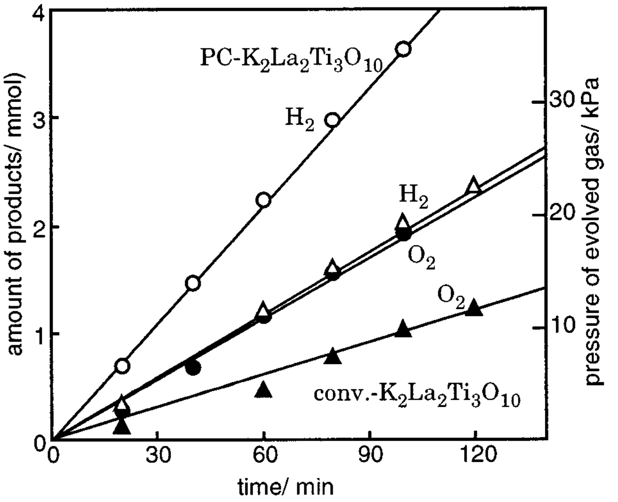

Figure 7. Time course of gas evolution over the PC−$K_2La_2Ti_3O_{10}$/Ni catalyst (○, H_2; ●, O_2) and the conventional $K_2La_2Ti_3O_{10}$/Ni catalyst (△, H_2; ▲, O_2): 1 g of catalyst; 300 cm^3 of aqueous KOH (0.1 M); high-pressure Hg lamp (450 W) light source; inner irradiation type quartz reaction cell.

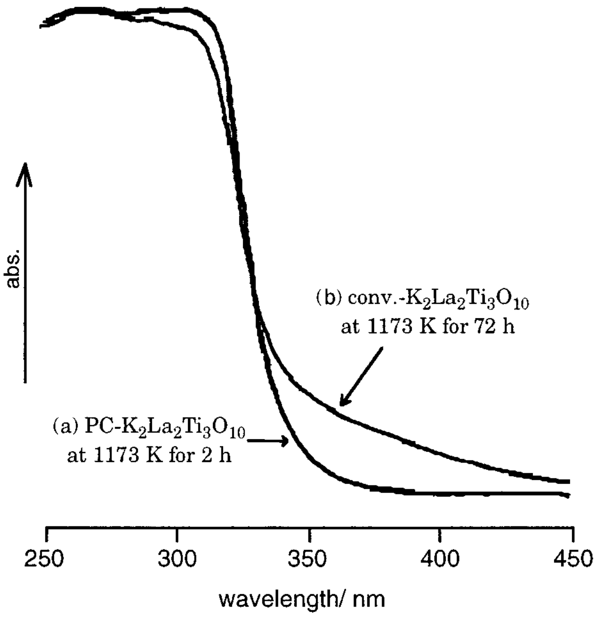

Figure 8. UV−vis DR spectra of $K_2La_2Ti_3O_{10}$: (a), the PC−$K_2La_2Ti_3O_{10}$ prepared at 1173 K for 2 h; (b), the conventional-$K_2La_2Ti_3O_{10}$ prepared at 1173 K for 72 h.

Photocatalytic Activity. Table 2 lists the photocatalytic activities of water decomposition upon Ni (3 wt %) loaded $K_2La_2Ti_3O_{10}$ prepared by the PC method (from the "K/La/Ti = 4/2/3" precursor) at temperatures between 1073 and 1223 K with their BET surface areas measured by N_2 adsorption at 77 K. The highest activity was achieved by the sample calcined at 1173 K for 2 h, and the photocatalytic activity decreased with the increasing the preparation temperature from 1173 to 1223 K. The decrease of the activity is regarded as being due to the decrease of the surface area. On that account, the samples prepared at lower calcination temperatures (1073 K for 12 h and at 1123 K for 2 h) were expected to exhibit higher activities because of their much larger surface area than that prepared at 1173 K for 2 h. However, the samples prepared at 1073 and 1123 K show lower photocatalytic activity. Figure 5 shows the SEM photographs of the catalysts prepared by the PC method at temperatures between 1073 and 1223 K. The morphology of the sample calcined at 1073 K for 12 h (Figure 5a) was granular, and individual particles could not be distinguished, while individual particles of the sample calcined at 1123 K for 2 h (Figure 5b) were clearly distinguishable with uneven surface. In the case of the samples calcined at 1173 and 1223 K for 2 h (Figure 5c,d), a smooth surface and a square shape were observed for each particle. From the SEM measurements, the products calcined at 1073 and 1123 K are not considered to be synthesized into the complete structure of $K_2La_2Ti_3O_{10}$. The UV−vis DR spectra of the powders prepared at temperatures between 873 and 1223 K are shown in Figure 6 in a wavelength region of 250−450 nm. As shown in the XRD in Figure 3b, the product prepared at 873 K for 2 h (Figure 6a) is $La_{2/3}TiO_3$. The products prepared at 1073 K for 12 h and 1123 K for 2 h (Figure 6b,c, respectively) contain an absorption band similar to $La_{2/3}TiO_3$ at about 350−400 nm. On the other hand, both of the products prepared at higher temperatures (1173 K for 2 h and 1223 K for 2 h, shown in Figure 6d,e, respectively) show the same absorption spectra. Therefore, the products prepared at 1073 K for 12 h and at 1123 K for 2 h contain a $La_{2/3}TiO_3$ phase that is an inactive phase for photocatalytic water splitting (as indeed revealed by the XRD; see Figure 3c,d) and show photocatalytic activities much less than expected from those relatively large surface areas. Furthermore, the photocatalytic activity is governed by their surface area for genuine crystals of $K_2La_2Ti_3O_{10}$ practically free from any other phases.

The photocatalytic activities of the catalysts prepared by the solid-state reaction method, and each BET surface areas is summarized in Table 3. In the case of the catalysts prepared at 1323 K for 48 h, the catalyst obtained from the mixture contained 30% excess of potassium (K/La/Ti = 2.6/2/3) exhibits higher activity than that obtained from the stoichiometric mixture (K/La/Ti = 2/2/3). In comparison of their XRD results (as shown in Figure 4e,b, respectively), the former shows pure $K_2La_2Ti_3O_{10}$ phase in contrast to the latter. Comparing the catalyst prepared by heating the "K/La/Ti = 2.6/2/3" mixture at 1173 K for 72 h with that prepared at 1323 K for 48 h, the former has a higher activity than the latter as expected from the larger surface area of the former.

Figure 7 shows the time course of H_2 and O_2 evolution of the most active catalysts prepared by the PC method at 1173 K for 2 h and that prepared by the conventional solid-state reaction method at 1173 K for 72 h. The photocatalytic activity of the PC−Ni/$K_2La_2Ti_3O_{10}$ is double that of the conventional Ni/$K_2La_2Ti_3O_{10}$. The difference of the activity in both methods cannot be explained only by the surface areas because the difference in surface area is much smaller (5 and 4 $m^2\ g^{-1}$, respectively) than that in activity. UV−vis DR spectra of both powders are compared in Figure 8. The spectrum of the conventional $K_2La_2Ti_3O_{10}$ has a shoulder peak at a wavelength of about 350−450 nm. The absorption band could be observed in all powders synthesized through the conventional solid-state reaction method. Although the absorption band could not be assigned because there was no impurities in the conventional $K_2La_2Ti_3O_{10}$ as shown in the XRD results (Figure 4d,e), a defect such as a nonstoichiometric part was considered to exist, which might act as recombination centers for photogenerated electron−hole pairs.

In summary, this study has exhibited the advantage of the PC method to prepare a highly active photocatalyst compared with the conventional solid-state reaction. This method is expected to be applicable for the synthesis of other mixed metal oxide catalysts with high activities.

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