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Photocatalytic Decomposition of Water on Spontaneously Hydrated Layered Perovskites

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Photocatalytic decomposition of H_2O is the subject which has been studied from the viewpoint of photon energy conversion. The goal of such studies is to provide a system in which H_2 and O_2 evolve efficiently and steadily under visible light irradiation. So far, no photocatalyst has been found to work in such a condition. Actually, it is possible to electrolyze water using a wet-type solar cell,[1] but the construction of a photocatalytic system for the simultaneous and efficient evolution of H_2 and O_2 persists as an attractive challenge.

Recently, the application of several photocatalytic systems containing oxide powders to an overall water splitting have been reported.[2−8] The present authors have reported that the photocatalytic systems based on some ion-exchangeable layered oxides is advantageous in several respects as compared to the so-called "bulk" type photocatalysts such as TiO_2.[6−8] Typically, $K_4Nb_6O_{17}$ and $Rb_4Nb_6O_{17}$ catalysts with a Ni loading of 0.1 wt % were found to decompose the intercalated H_2O molecules to H_2 and O_2 under bandgap (3.3 eV) irradiation.[7,8] These niobates have a unique structure in that two different type of interlayer spaces exist alternately on the two sides of a negatively charged niobate sheet and the intercalated H_2O molecules are efficiently decomposed due to this structural characteristic.[9] However, subsequent attempts to extend the absorption edge of the system into the visible region have not been successful because of the difficulty in modification of the niobate sheet.

We have also revealed that a family of layered perovskite type niobates that contain alkaline metal cations at the interlayer space, $AB_2Nb_3O_{10}$ (A = K, Rb, Cs; B = Ca, Sr, Pb, etc.), were highly active photocatalysts for the evolution of H_2 from an aqueous solution of methanol when protons are substituted for alkaline metal cations. The H^+-exchanged forms are hydrated although the original forms of these perovskites are not hydrated. The much higher activity of the H^+-exchanged form by more than 3 orders in acidic solution was, therefore, ascribed to the availability of the interlayer space as reaction sites.[6,10] However, an alkaline condition is usually preferred or indispensable for the decomposition of H_2O into H_2 and O_2 probably to facilitate O_2 formation.[5,7,8,11] The layered perovskites examined before were not hydrated in such an alkaline condition. More importantly, this family has so much variety in composition and structure, and various modification is also facile. A layered perovskite photocatalyst, $RbPb_2Nb_3O_{10}$, actually shows visible light responses.[10,12] The above-described considerations lead us to infer as promising to adopt the ion-exchangeable layered perovskites which get hydrated in an alkaline condition. Reported here is the first successful result of the strategy; the ion-exchangeable layered perovskites with a general formula of $A_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ (A = interlayer cations such as K, Rb, Cs; $x = 0, 0.5, 1$)[13−15] are presented as photocatalysts for water decomposition. Photons are absorbed in the perovskite layers containing Ti^{4+}/Nb^{5+} cations to generate photoexcited conduction electrons and valence holes. These electrons and holes reduce H_2O into H_2 and oxidize into O_2, respectively.

The $A_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ substances were prepared according to the method described by Goparakrishnan and co-workers who worked out the intercalation behaviors as well as the structure.[13−15] Ni-loaded photocatalyst was prepared by the impregnation of the powder with an aqueous $Ni(NO_3)_2$ solution followed by calcination in air at ca. 575 K for 20 min. The catalyst was next activated by H_2 reduction at 773 K for 2 h and subsequent O_2 reoxidation at 473 K for 1 h.[7,8,11] The catalyst (1.0 g) suspended in distilled water (330 mL) by magnetic stirring and photocatalytic reaction was carried out in a closed gas circulation system using a high-pressure Hg lamp (450 W) placed in an inner irradiation type quartz reaction cell. Bandgaps estimated from UV−vis diffuse reflectance spectra are about 3.4−3.5 eV for all compounds.

The optimum activities and conditions of the catalysts examined and the number of hydration determined by thermogravimetric analysis are summarized in Table 1. Some of the catalysts evolved H_2 and O_2 without Ni loading but the activity was enhanced markedly by Ni loading in each case. The role of loaded Ni is to facilitate the H_2 evolution as an efficient catalysis of recombinative H_2 formation.[9,11] Some of the catalysts exhibited even higher activities by the addition of AOH (A = K, Rb, Cs) as is often the case in the photocatalytic

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Table 1. Photocatalytic Activities of Various Layered Perovskites and Hydration Numbers

	rate of gas evolution/μmol h^{-1}		optimum condition			
catalyst	H_2	O_2	Ni-loading/wt %[a]	AOH/mol L^{-1} [b]	pH	hydration no. *n*[c]
$K_2La_2Ti_3O_{10}$	444	221	3	0.1	12.8	1.0
$Rb_2La_2Ti_3O_{10}$	869	430	4	0.1	12.8	1.1
$Rb_{1.5}La_2Ti_{2.5}Nb_{0.5}O_{10}$	725	358	5	0.1	12.6	0.9
$RbLa_2Ti_2NbO_{10}$	79	30	0.3	0.1	12.8	0
$Cs_2La_2Ti_3O_{10}$	700	340	3	0	10.5	3.5
$Cs_{1.5}La_2Ti_{2.5}Nb_{0.5}O_{10}$	540	265	4	0	10.4	2.0
$CsLa_2Ti_2NbO_{10}$	115	50	0.3	0	8.5	0

[a] Amount of loaded Ni. [b] Concentration of aqueous AOH (A = K, Rb, Cs) solution. [c] The number of hydration in the formula of $A_{2-x}La_2Ti_{3-x}Nb_xO_{10}\cdot nH_2O$. Reaction condition; catalyst 1.0 g; H_2O 320 mL; high-pressure mercury lamp (450 W); an inner irradiation type quartz reaction cell.

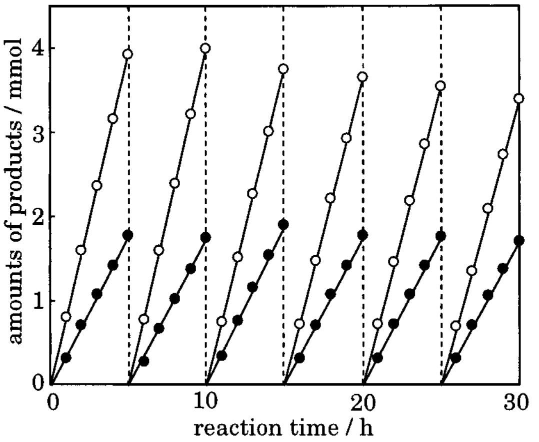

Figure 1. Time course of H_2 and O_2 evolution from aqueous RbOH solution (0.1 M) over Ni (4.0 wt %)−$Rb_2La_2Ti_3O_{10}$ catalyst. The gas phase was evacuated at every for 5 h of reaction and the amount of evolved H_2 and O_2 are plotted by open and filled circles, respectively. Reaction conditions; catalyst 1.0 g; H_2O 330 mL; a high-pressure mercury lamp (450 W); an inner irradiation type quartz cell.

decomposition of H_2O.[5,11] Typically, Ni (4.0 wt %)−$Rb_2La_2Ti_3O_{10}$ catalyst in the 0.1 M aqueous RbOH solution (pH = ca. 12.8) showed the highest activity of all the catalysts examined, and the time course of H_2 and O_2 evolution is depicted in Figure 1 where the amount of evolved H_2 and O_2 gases are plotted by open and closed circles, respectively, against reaction time. H_2 and O_2 evolved steadily and after 5 h of reaction the total pressure of a closed circulation system of ca. 250 mL volume reached about 450 Torr (1 Torr = 133 Pa), and the gas phase was evacuated at every 5 h of reaction while the reaction was continued for 30 h as shown in the Figure 1. For the use of 1.3 mmol of $Rb_2La_2Ti_3O_{10}$ and 0.7 mmol of Ni, the amount of evolved H_2/O_2 gases reached more than 20/10 mmol after 30 h of irradiation, which confirmed the catalytic cycle. The quantum efficiency was ca. 5% at around 330 nm as estimated by comparing to the value given previously for the reaction using Ni (0.1 wt %)-$K_4Nb_6O_{17}$.[8]

A partial substitution of Ti^{4+} by Nb^{5+} leads to the decrease in the negative charge density of the perovskite layer and thus to the decrease of the number of alkaline metal cations located to maintain the charge balance at the interlayer space. As it turned out, the interlayer space was not hydrated when one-third of Ti^{4+} was replaced by Nb^{5+}, $ALa_2Ti_2NbO_{10}$ (x = 1.0), although hydration took place for $A_2La_2Ti_3O_{10}$ and $A_{1.5}La_2Ti_{2.5}Nb_{0.5}O_{10}$ as seen from Table 1. The activity of $ALa_2Ti_2NbO_{10}$ catalyst was lower by about 1 order than the others, while there is not much difference between $A_2La_2Ti_3O_{10}$ and $A_{1.5}La_2Ti_{2.5}Nb_{0.5}O_{10}$ catalysts. The partial substitution by Nb does not lead to so many changes in the characters of catalysts such as bandgap value or particle size which should affect on the photocatalytic activity. Therefore, it is inferred that higher activity of the latter two catalysts derives from the availability as reaction sites of the interlayer. It seems that layered perovskites which hold larger amount of alkaline metal cations at the interlayer space facilitate the hydration. Increase of negative charge density of the layer enables to increase the amount of alkaline metal cations at the interlayer space. This indicates a useful guiding principle to develop photocatalysts for an efficient water splitting with a hydrated layered perovskite type structure.

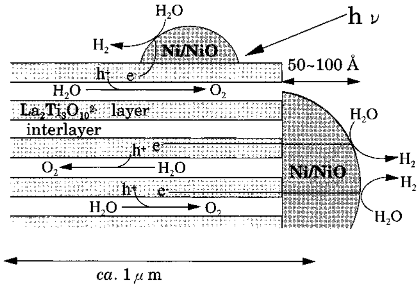

Figure 2. Schematic view of the reaction mechanism of H_2O decomposition on layered perovskite photocatalyst.

As seen from Table 1, the $A_2La_2Ti_3O_{10}$ and $A_{1.5}La_2Ti_{2.5}Nb_{0.5}O_{10}$ catalysts required larger amounts of Ni loading (3.0−5.0 wt %) for the optimum activities than that (0.1 wt %) of $K_4Nb_6O_{17}$.[7] Most of the loaded Ni was found to exist as the particles of about 100−200 Å at the external surface of the catalyst, which is in distinct contrast to the case for the previously studied Ni−$K_4Nb_6O_{17}$ catalyst.[9] This indicates that the reaction mechanisms on these layered perovskites are different from that of $K_4Nb_6O_{17}$. We tentatively propose from the morphology that H_2 evolves on Ni particles at the external surface and O_2 evolves at the interlayer space. Schematic view of the reaction mechanism of H_2O decomposition is shown in Figure 2. The details of the reaction mechanism of H_2O decomposition on Ni-loaded perovskites is now under investigation.

An efficient overall water splitting was attained by a novel series of layered perovskite type materials. This is the first report on the use of ion-exchangeable layered compounds with only one type of interlayer space as catalysts for an overall water splitting. The importance of the hydration was demonstrated indicating the role of the interlayer space as reaction sites.

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