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Effect of Chromium Addition for Photocatalytic Overall Water Splitting on Ni–$K_2La_2Ti_3O_{10}$

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A third component was added to the Ni–$K_2La_2Ti_3O_{10}$ photocatalyst in order to improve the photocatalytic activity. Introduction of chromium to Ni–$K_2La_2Ti_3O_{10}$ as a third component was found to show promising results among the components examined. Cr–Ni–$K_2La_2Ti_3O_{10}$ showed a higher photocatalytic activity for water decomposition than Ni–$K_2La_2Ti_3O_{10}$ catalyst. The highest activity was obtained by the loading of 0.5 wt% of chromium to Ni (3.0 wt%)–$K_2La_2Ti_3O_{10}$. Moreover, chromium addition was also found to improve the durability of catalytic activity against long periods of photoirradiation.

Key Words: **chromium addition; photocatalysis of water; layered perovskite.**

INTRODUCTION

Photodecomposition of water on heterogeneous photocatalysis has been extensively studied from the viewpoint of photon energy conversion (1–5). Recently, we have reported that a layered perovskite-type compound $K_2La_2Ti_3O_{10}$ exhibits a high activity for overall water splitting by nickel-loading with proper pretreatment (6, 7). Successful overall water splitting has never been performed by modification with metals other than nickel over $K_2La_2Ti_3O_{10}$ catalyst. Remarkable enhancement observed upon nickel modification holds true in some titanates and niobates (8, 9). Therefore, modification by nickel is, so far, the best method known to enhance the photocatalytic activity of $K_2La_2Ti_3O_{10}$ as well as some typical photocatalyst toward overall water decomposition. Most of the successful photocatalytic overall water splitting was performed on the system of semiconductor powder loaded with small metal or metal oxide particles as a co-catalyst on the surface. Examples of effective loading materials have been limited (2, 3, 8, 10, 11), and this is important to promote the field of photocatalytic water decomposition. The purpose of this study is to improve the photocatalytic activity of Ni–$K_2La_2Ti_3O_{10}$ catalyst by the addition of a third component.

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EXPERIMENTAL

$K_2La_2Ti_3O_{10}$ was prepared by conventional ceramics techniques (12). K_2CO_3, La_2O_3, and TiO_2 powders in a molar ratio of 1.1 : 1 : 3 were mixed by mechanical grinding in a motor. The mixture was then calcined at 1223 K for 2 h followed by grinding and recalcination at 1323 K for 40 h. Loading of nickel and another metal was carried out by coimpregnation methods. $K_2La_2Ti_3O_{10}$ was immersed into an aqueous solution that contained the required amount of $Ni(NO_3)_2$ and other metal nitrate or chloride. The solution was then evaporated to dryness in a water bath followed by heating in air at ca. 573 K for 20 min. The catalyst was then activated by H_2 reduction at 773 K for 2 h and subsequent oxidation by O_2 at 473 K for 1 h in a closed gas circulation system (6, 7). Loaded nickel has a complicated structure consisting of metallic and oxide parts after this treatment (8, 9). Therefore, the catalyst with this pretreatment should be described as MO_x–NiO_y–$K_2La_2Ti_3O_{10}$, but we simply refer to it as M–Ni–$K_2La_2Ti_3O_{10}$. Photocatalytic reaction was carried out in an air-free closed gas circulation system with an inner irradiation-type reactor. Catalyst (1.0 g) was dispersed in an aqueous KOH solution (0.1 M, 320 ml) by magnetic stirring and was irradiated under an Ar atmosphere (about 50 Torr) by a high-pressure Hg lamp (450 W, $>$190 nm). Amounts of evolved gases were analyzed by gas chromatography (molecular sieve 5A column, Ar carrier, thermal conductivity detector) through a gas sampler (ca. 3 ml) which was directly connected to the reaction system to avoid any contamination from air.

RESULTS AND DISCUSSION

Effect of the Addition of Various Metal Oxides onto Ni–$K_2La_2Ti_3O_{10}$

Various kinds of metals were introduced to the Ni–$K_2La_2Ti_3O_{10}$ catalyst as a third component in order to improve the photocatalytic activity of H_2O decomposition. The third component was added to the impregnation solution as described above. Table 1 shows the rates of H_2 and

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TABLE 1

Photocatalytic Activities of Various Third Components Added to Ni–$K_2La_2Ti_3O_{10}$

Third component	Amounts of products[a]/μmol	
	H_2	O_2
None	3040	1530
Cr	3270	1650
Mn	80	30
Fe	24	10
Co	628	0
Cu	782	23
Ru	670	8
Ag	893	441
Ce	1290	623
Sm	153	20
Pb	372	0

[a] Total amounts of H_2 and O_2 evolved after 6 h of photoirradiation from the beginning of the reaction.

O_2 evolution when different transition metals were added as a third component. The amount of the third component was 0.05 wt% versus $K_2La_2Ti_3O_{10}$ in each case. The amount of nickel loading was 3.0 wt% against $K_2La_2Ti_3O_{10}$, where the optimum activity was previously obtained. Introduction of a third component to Ni–$K_2La_2Ti_3O_{10}$ resulted in a decrease of photocatalytic activity in most cases. A successful overall water splitting has never been performed over $K_2La_2Ti_3O_{10}$ modified by metals other than nickel, and thus the combination of $K_2La_2Ti_3O_{10}$ and nickel is particularly effective for overall water decomposition. Moreover, photocatalytic activities of $K_2La_2Ti_3O_{10}$ loaded with metals other than nickel are usually lower than that of the original $K_2La_2Ti_3O_{10}$. Therefore, incorporation of small amounts of other transition metals as a third component might also play a similar role. However, as can be seen from Table 1, Cr–Ni–$K_2La_2Ti_3O_{10}$ gave an interesting result wherein the photocatalytic activity of water decomposition was higher than that of Ni–$K_2La_2Ti_3O_{10}$. In order to learn the behavior of Cr–Ni–$K_2La_2Ti_3O_{10}$, further study on this catalyst was carried out.

Effect of the Method for Cr and Ni Loading on $K_2La_2Ti_3O_{10}$

Photocatalytic activities of Cr–Ni–$K_2La_2Ti_3O_{10}$ prepared by various impregnation methods were examined. The above-described Cr–Ni–$K_2La_2Ti_3O_{10}$ was prepared by coimpregnation methods; the two components were simultaneously impregnated from an aqueous solution containing both chromium and nickel nitrate. In addition to the coimpregnation method, reimpregnation methods were examined. For the reimpregnation method, impregnation procedures were separately carried out for the two components. Nickel impregnation was done on $K_2La_2Ti_3O_{10}$, and chromium-impregnation was subsequently done on nickel-impregnated $K_2La_2Ti_3O_{10}$. Here, this procedure is referred to as a normal reimpregnation method. In contrast to the normal reimpregnation method, a reverse order reimpregnation method was also carried out wherein chromium impregnation precedes nickel impregnation. Photocatalytic activities of water decomposition over Cr–Ni–$K_2La_2Ti_3O_{10}$ prepared from various impregnation methods are summarized in Table 2. The catalyst prepared by the coimpregnation method showed a higher activity than those prepared from reimpregnation methods. Nickel and chromium are more homogeneously mixed by coimpregnation methods compared with the two reimpregnation methods. During the evaporation of aqueous $Ni(NO_3)_2$ solution, Ni^{2+} ions are precipitated as $Ni(OH)_2$ due to the alkaline characteristics of aqueous $K_2La_2Ti_3O_{10}$ suspensions. For the procedure of coimpregnation of chromium and nickel, both Cr^{3+} and Ni^{2+} ions should be precipitated as hydroxides based on the pH values of aqueous $K_2La_2Ti_3O_{10}$ suspensions. Comparative rates of precipitation are different between the two kinds of ions, and thus the distribution of loaded chromium and nickel might not be homogeneous enough to form an atomic order array. However, the fact is that prominent differences in the photocatalytic activity were observed for each impregnation method. This indicates that the structure of the loaded co-catalyst, especially concerning the distribution of chromium and nickel, should be an important factor in determining the effect of the addition of chromium to enhance the photocatalytic activity of water decomposition. In any case, since coimpregnated Cr–Ni–$K_2La_2Ti_3O_{10}$ showed the highest activity among the catalysts examined, coimpregnation methods were employed for the following experiments.

Photodecomposition of Water by Cr–Ni–$K_2La_2Ti_3O_{10}$

The dependence of the photocatalytic activity of water decomposition on the amount of chromium addition to nickel-loaded $K_2La_2Ti_3O_{10}$ was studied as shown in Fig. 1.

TABLE 2

Photocatalytic Activities of Water Decomposition over Cr (0.05 wt%)–Ni (3.0 wt%)–$K_2La_2Ti_3O_{10}$ Prepared by Several Impregnation Methods

Loading method	Rates of gas evolution/μmol · h^{-1}	
	H_2	O_2
Coimpregnation	542	265
Normal reimpregnation	363	169
Reverse order reimpregnation	428	206

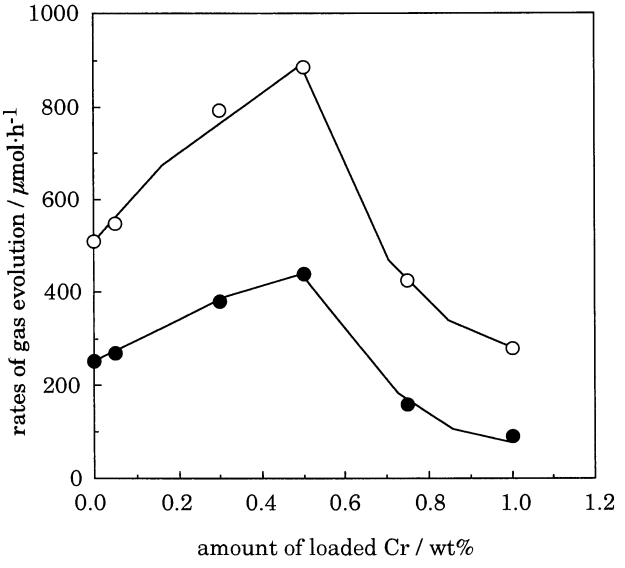

FIG. 1. Dependence of the activity of photocatalytic decomposition of water over Cr–Ni–$K_2La_2Ti_3O_{10}$ catalyst upon the amount of loaded Cr. Open circle, H_2; closed circle, O_2; 1.0 g of catalyst; 320 ml of aqueous KOH solution (0.1 mol·l^{-1}); high-pressure Hg lamp (450 W); inner irradiation type quartz reaction cell.

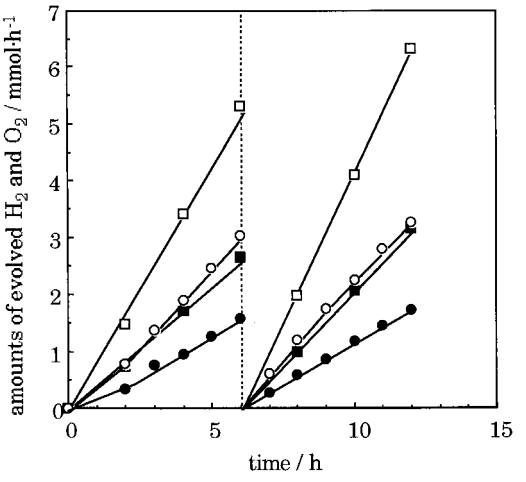

FIG. 2. Time courses of H_2 and O_2 evolution over Cr (0.5 wt%)–Ni (3.0 wt%)–$K_2La_2Ti_3O_{10}$ and Ni (3.0 wt%)–$K_2La_2Ti_3O_{10}$. Open square, H_2 of Cr–Ni–$K_2La_2Ti_3O_{10}$; filled square, O_2 of Cr–Ni–$K_2La_2Ti_3O_{10}$; open circle, H_2 of Ni–$K_2La_2Ti_3O_{10}$; filled circle, O_2 of $K_2La_2Ti_3O_{10}$; 1.0 g of catalyst; 320 ml of aqueous KOH solution (0.1 mol·l^{-1}); high-pressure Hg lamp (450 W); inner irradiation type quartz reaction cell.

Optimum activity was obtained with 0.5 wt% chromium loading (Cr : Ni = 1 : 6 and 1 : 5.3 in gravimetric and molar ratios, respectively). The rate of H_2 and O_2 evolution increased with the amount of loaded chromium up to 0.5 wt%, while it decreased gradually at loading higher than 0.5 wt%. The maximum photocatalytic activity was obtained for Cr (0.5 wt%)–Ni (3.0 wt%)–$K_2La_2Ti_3O_{10}$ and was higher than that of Ni (3.0 wt%)–$K_2La_2Ti_3O_{10}$ by about 1.7 times. Here, it is obvious that chromium is a promising component to enhance the photocatalytic activity of Ni (3.0 wt%)–$K_2La_2Ti_3O_{10}$. Cr (0.5 wt%)–$K_2La_2Ti_3O_{10}$ was also photocatalytically active toward water splitting, but the rates of H_2 and O_2 were lower than those of Ni (3.0 wt%)–$K_2La_2Ti_3O_{10}$ as shown in Table 3. Only the loading of chromium to $K_2La_2Ti_3O_{10}$ was not very effective to enhance the photocatalytic activity. The effect of chromium addition to enhance the photocatalytic activity appears when nickel exists together with chromium.

TABLE 3

Photocatalytic Activities of Water Decomposition over Cr and/or Ni-loaded $K_2La_2Ti_3O_{10}$

Loaded material	Rates of gas evolution/μmol·h^{-1}	
	H_2	O_2
Ni (3.0 wt%)	507	253
Cr (0.5 wt%)–Ni (3.0 wt%)	885	442
Cr (0.5 wt%)	191	18

Photocatalytic decomposition of water over Cr (0.5 wt%)–Ni (3.0 wt%)–$K_2La_2Ti_3O_{10}$ catalyst was continued for a long period with intermediative evacuation every 6–8 h. A portion of the time courses of H_2 and O_2 evolution on both catalysts is shown in Fig. 2. Moreover, the rates of H_2 and O_2 evolution over Cr (0.5 wt%)–Ni (3.0 wt%)–$K_2La_2Ti_3O_{10}$ as well as Ni–$K_2La_2Ti_3O_{10}$ in each run are plotted against irradiation time in Fig. 2. H_2 and O_2 evolved steadily and gas analysis was done every 2 h. The Cr (0.5 wt%)–Ni (3.0 wt%)–$K_2La_2Ti_3O_{10}$ system reached a maximum rate of 1186.6 μmol·h^{-1} for H_2 evolution after 18 h of irradiation, and then it gradually decreased. As shown in Fig. 3, the present system gave higher rates of H_2 and O_2 evolution by about 2 times compared to those of Ni–$K_2La_2Ti_3O_{10}$ system. In the case of Ni–$K_2La_2Ti_3O_{10}$, it took about 86 h to decrease its catalytic activity up to one-third of its maximum, while it took 124 h to reach one-third of the maximum activity in the case of Cr–Ni–$K_2La_2Ti_3O_{10}$. Therefore, it is clear that chromium addition to Ni–$K_2La_2Ti_3O_{10}$ catalyst has another effect: to prolong the lifetime of catalysts compared with Ni–$K_2La_2Ti_3O_{10}$.

No detailed structural information about the Cr–Ni cocatalyst was obtained by means of microscopic and spectroscopic analysis such as TEM, EDS, and XPS because of the small amount of chromium. Most of the loaded nickel was deposited as particles of 10–20 nm on the external surface of $K_2La_2Ti_3O_{10}$ in the case of Ni–$K_2La_2Ti_3O_{10}$, and the nickel particle has a structure consisting of metallic and oxide parts after the treatment with R773-O473 (7, 8). Loaded chromium might be dispersed on the surface of a $K_2La_2Ti_3O_{10}$ particle similarly to nickel. Since chromium tends to be more easily oxidized than nickel,

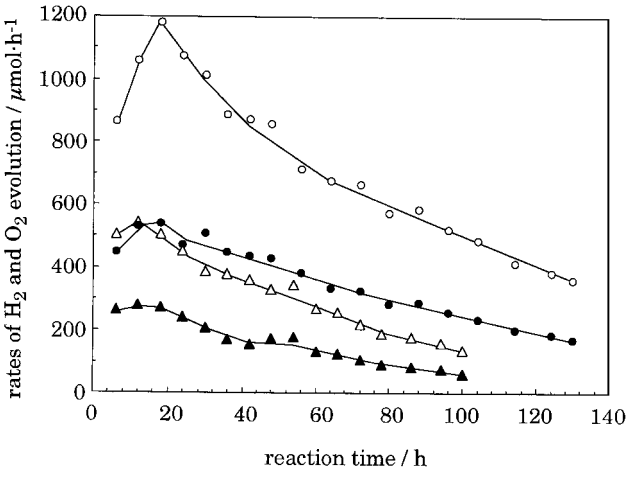

FIG. 3. Time courses of the rates of H_2 and O_2 evolution over Ni (3.0 wt%)–$K_2La_2Ti_3O_{10}$ and Cr (0.5 wt%)–Ni (3.0 wt%)–$K_2La_2Ti_3O_{10}$. Open circle, H_2 of Cr–Ni–$K_2La_2Ti_3O_{10}$; filled circle, O_2 of Cr–Ni–$K_2La_2Ti_3O_{10}$; open triangle, H_2 of Ni–$K_2La_2Ti_3O_{10}$; filled triangle, O_2 of Ni–$K_2La_2Ti_3O_{10}$; 1.0 g of catalyst; 320 ml of aqueous KOH solution (0.1 mol·l^{-1}); high-pressure Hg lamp (450 W); inner irradiation type quartz reaction cell.

loaded chromium should exist as Cr_2O_3 after the treatment with R773-O473. The fact that coimpregnated catalyst showed higher activity than both normal and reverse-order reimpregnated catalysts is attributed to mixed oxide composed of chromium and nickel. Moreover, Cr–$K_2La_2Ti_3O_{10}$ showed considerably lower activity than that of Ni–$K_2La_2Ti_3O_{10}$, indicating that chromium does not work as an active site. One possible effect of chromium is to assist the role of nickel as a promoter to form H_2 by changing the electronic property of nickel. The addition of univalent metal cations such as Li^+ and Ag^+ to NiO as *p*-type semiconductor promotes O_2 adsorption while the addition of trivalent metal cations such as Cr^{3+} decreases O_2 adsorption (13). O_2 adsorption on NiO can obstruct H_2 formation. Although the role of chromium is now under investigation, chromium in mixed oxide co-catalyst might improve H_2 evolution, preventing the adsorption of O_2.

CONCLUSIONS

In summary, loading of small amounts of chromium to Ni–$K_2La_2Ti_3O_{10}$ by means of a coimpregnation method was found to have two promising effects on photocatalytic water decomposition. About 2 times higher photocatalytic activity of water decomposition was obtained over Cr (0.5 wt%)–Ni (3.0 wt%)–$K_2La_2Ti_3O_{10}$ compared with that of Ni (3.0 wt%)–$K_2La_2Ti_3O_{10}$. Furthermore, Cr–Ni–$K_2La_2Ti_3O_{10}$ catalyst showed durability for longer periods of irradiation than Ni–$K_2La_2Ti_3O_{10}$. The role of added chromium is not yet clearly understood, and further studies have to be done to identify the detailed structure of the Cr–Ni–$K_2La_2Ti_3O_{10}$ catalyst and to clarify the role of added chromium.

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