IMPROVEMENT OF NICKEL-LOADED $K_4Nb_6O_{17}$ PHOTOCATALYST FOR THE DECOMPOSITION OF H_2O

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The activity of a Ni-loaded $K_4Nb_6O_{17}$ photocatalyst for an overall water splitting was enhanced by the addition of alkaline hydroxide (KOH, NaOH) into the aqueous impregnation solution. The quantum efficiency was 5.3% (330 nm) at the optimum condition.

1. Introduction

An overall water splitting into H_2 and O_2 on heterogeneous photocatalysts has been the subject of extensive work from the view point of photon energy conversion and several systems based on TiO_2 [1,2] or $SrTiO_3$ [3,4] powders have been recognized to be able to proceed the reaction. The quantum efficiencies at the steady state reaction condition of those systems, however, remained rather low, ca. 1%, although a considerably high efficiency (ca. 30%) was reported under a transient condition [5].

Recently, we reported that an ion-exchangeable layered compound, $K_4Nb_6O_{17}$ with Ni loading showed a unique activity for an overall water splitting, and the quantum efficiency at 330 nm was ca. 3.5% [6].

It is well-known that a high quantum efficiency of H_2 or O_2 evolution is obtained in an aqueous solution containing a socalled sacrificial reagent. In most of those systems, however, only a small or no amount of energy conversion from photon to chemical one occurs. Therefore, to increase the quantum efficiency of an overall water splitting which is accompanied by a large energy conversion (56.7 kcal/mol) is a difficult but significant problem to be solved.

The purpose of this study is improving Ni-loaded $K_4Nb_6O_{17}$ photocatalyst to obtain a quantum efficiency higher than that of one previously reported. Consequently the quantum efficiency of more than 5% at 330 nm was achieved with a good reproducibility at the steady state reaction condition.

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2. Experimental

$K_4Nb_6O_{17}$ powder was prepared from Nb_2O_5 (MITUIKINZOKU) and K_2CO_3 (Asahi Glass, Co.) at 1573 K in air and the crystal structure was confirmed by XRD. $K_4Nb_6O_{17}$ catalysts loaded with metal oxides were prepared by the impregnation method; $K_4Nb_6O_{17}$ was added in an aqueous solution which contained the required amount of $Ni(NO_3)_2$ and other metal nitrate (or metal hydroxide). Then the catalyst was calcined at 550 K in air for 1 h after drying the aqueous solution on a water bath. The catalyst was typically pretreated as follows; the catalyst was reduced by H_2(ca. 40 kPa) at 773 K for 2 h and then was oxidized by O_2 (ca. 16 kPa) at 473 K for 1 h.

Photocatalytic reactions were carried out in a closed gas circulation system as previously reported [3]. An inner irradiation reaction cell, in which a catalyst (1 g) was suspended by a magnetic stirrer in distilled water, was degassed completely and then Ar (ca. 16 kPa) was introduced. The cell was irradiated using a high pressure mercury lamp (USHIO UM-452, 450 W). Evolved gases were analyzed by gas chromatography (TCD, MS 5A, Ar carrier) which was calibrated using pure H_2 and O_2 gases in a closed gas circulation system. The quantum efficiency was determined by a chemical actinometry using $(NH_3)_3Fe(COO)_3.3H_2O$, and Xe lamp (USHIO 500W) and a monochrometer (JOBIN).

3. Results and discussion

1. EFFECT OF ADDITION OF VARIOUS METAL OXIDES (OR HYDROXIDES) ONTO Ni-LOADED $K_4Nb_6O_{17}$ CATALYST

At first we tried to improve the efficiency of an Ni-loaded $K_4Nb_6O_{17}$ catalyst by adding a third component into the impregnation solution as mentioned above. Table 1 shows the rates of H_2 and O_2 evolution when various metal oxides (0.05 wt%) or hydroxides were added to NiO(0.1 wt%)-$K_4Nb_6O_{17}$. A Ni-loaded $K_4Nb_6O_{17}$ catalyst was fully characterized by means of various spectroscopic methods (XPS, EXAFS, TEM etc.) in our previous study, and it was revealed that an active catalyst contains ultra fine nickel metal particles (ca. 5 Å) at the interlayer space I of $K_4Nb_6O_{17}$ [9]. On the other hand, the catalysts studied here were not characterized yet. Therefore, since we can not identify the forms of nickel or other metal components in the present catalysts, we used hydroxide or oxide forms of those components in the table and the text below as a convenience. It was found that in most cases the rates of H_2 and O_2 evolutions decreased more or less although the ratio of evolved amounts of H_2 and O_2 was almost stoichiometric. In the cases of rhodium or palladium addition, the activity disappeared, which may be understood that loaded Rh or Pd exists as metallic particles at the external surface of the catalyst and they work as an efficient

Table 1
The rate of H_2 and O_2 evolution when various metal oxides (0.05 wt%) were added to NiO (0.1 wt%)-$K_4Nb_6O_{17}$ photocatalyst

metal oxide or hydroxide as the third component	rate of gas evolution [μmol/h]	
	H_2	O_2
none	69±5	34±3
LiOH	35	16
NaOH	58	27
NaOH (a)	74	35
KOH	60	29
KOH (a)	91	44
RbOH	56	26
CsOH	73	35
MgO	52	24
CaO	22	7
SrO	7	2
BaO	24	7
Al_2O_3	45	20
Cr_2O_3	46	19
Mn_3O_4	30	17
Fe_2O_3	6	3
Co_3O_4	25	11
CuO	23	7
ZnO	33	18
GaO	63	29
Y_2O_3	25	11
RuO_2 (b)	45	18
Rh_2O_3 (b)	2	0
PdO (b)	2	0
Ag_2O	18	7
CdO	68	33
In_2O_3	71	34
PtO (b)	36	16
PbO	33	14
Bi_2O_3	24	10
La_2O_3	22	8
CeO_2	16	6
Pr_2O_3	23	10
Nd_2O_3	22	10
Sm_2O_3	58	28
Dy_2O_3	60	26

Metal oxides and hydroxides prepared by a thermodecomposition of metal nitrate; except (a): prepared from hydroxide, (b): prepared from chloride.

catalyst for the reverse reaction to form H_2O from H_2 and O_2. It was found that in the cases of alkali hydroxide (NaOH, KOH etc.) or oxide addition, the rates of water decomposition slightly increased. As was found that KOH addition was effective for the enhancement of water decomposition over Ni-loaded $K_4Nb_6O_{17}$ photocatalyst, the effect of potassium loading was studied in more detail.

2. EFFECT OF POTASSIUM ADDITION

Figure 1 shows the dependence of the rates of H_2 and O_2 evolution over KOH-NiO (0.1 wt% or 1 wt%)-$K_4Nb_6O_{17}$ upon the amount of added potassium. Potassium was added as KOH or KNO_3 into the aqueous solution containing the relevant amount of $K_4Nb_6O_{17}$ and $Ni(NO_3)_2$ followed by drying up on a water bath and then calcination in air. The rate of H_2 and O_2 evolution over the catalyst prepared from KNO_3 decreased monotonously with the increase of the amount of added potassium, while those prepared from KOH showed a maximum activity at 0.1 wt% and 1 wt% of KOH addition for NiO (0.1 wt%)- and NiO(1wt%)-$K_4Nb_6O_{17}$, respectively. The atomic ratio of K to Ni was ca. 1.6 in both cases. The rates of H_2 and O_2 evolutions over KOH (0.1 wt%)-NiO(0.1 wt%)-$K_4Nb_6O_{17}$ were 124 μmol/h and 61 μmol/h under a full irradiation of a high pressure mercury lamp (450 W), and the quantum efficiency was estimated to be ca. 5.3% at 330 nm.

Figure 2 shows the time course of H_2 and O_2 evolution from distilled water over KOH (0.1 wt%)-NiO(0.1 wt%)-$K_4Nb_6O_{17}$ and NiO (0.1 wt%)-$K_4Nb_6O_{17}$ catalysts. It is clearly shown that H_2 and O_2 steadily evolves in a stoichiometric ratio in both catalysts and KOH addition enhances the rate of H_2O decomposition.

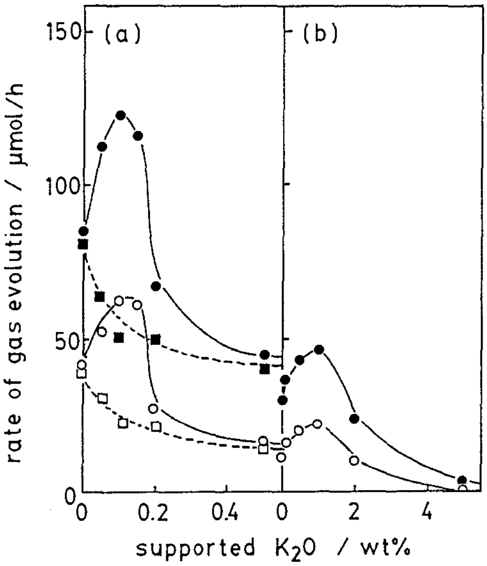

Fig. 1. Dependence of the rates of H_2 and O_2 evolution upon the amount of added K_2O over (a) KOH-NiO (0.1 wt%)-$K_4Nb_6O_{17}$ and (b) KOH-NiO (1 wt%)-$K_4Nb_6O_{17}$, ●: H_2 evolved, ○: O_2 evolved adding potassium as KOH, ■: H_2 evolved, □: O_2 evolved adding potassium as KNO_3.

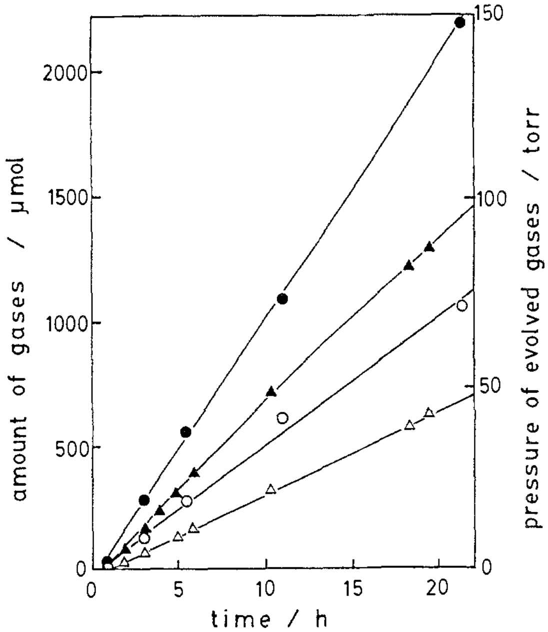

Fig. 2. Time course of H_2 and O_2 evolution from distilled water (300 ml) over KOH (0.1 wt%)-NiO(0.1 wt%)-$K_4Nb_6O_{17}$ (●: H_2, ○: O_2), and NiO (0.1 wt%)-$K_4Nb_6O_{17}$ (▲: H_2, △: O_2).

$K_4Nb_6O_{17}$ has a layered structure of niobium oxide sheets with interlayers where potassium ions located [7]. The interlayers are easily hydrated and potassium ions are replaced by various cations [8]. Nickel ions are possible to be substituted for K^+ ions during the impregnation process. As mentioned above, in an active catalyst of Ni-loaded $K_4Nb_6O_{17}$, loaded Ni exists as ultra fine metal particles (ca. 5 Å) at the interlayer spaces [9]. When KOH is added to aqueous nickel nitrate solution, it is expected that nickel ions form small cluster ions by the O^{2-} or OH^- bridge as follows [10];

When $K_4Nb_6O_{17}$ is immersed in the aqueous solution containing KOH, the nickel cluster ions are expected to be intercalated into the interlayer spaces of $K_4Nb_6O_{17}$ instead of K^+ ions. We believe that ultra fine Ni metal particles at the interlayer I act as H_2 recombination centers where photoexited electrons are transferred to H^+ ions. Therefore, it is supposed that the forms of nickel ions located at the interlayers after the impregnation procedure are different with or without KOH addition, and it would affect the activity for water decomposition even after the pretreatment. This argument is supported by the following facts; in both cases 0.1 wt% and 1 wt% nickel loading, the activity of the catalyst prepared from KOH reached the maximum values at the same K/Ni atomic ratio, i.e. 1.6. This might suggest that added KOH is consumed to form some cluster ions with Ni^+ ions. Furthermore, the activity increased by NaOH addition and not by KNO_3 and $NaNO_3$ addition, i.e. the alkaline addition is a necessary condition. The pH of the solutions were almost constant in any cases (pH = ca. 11).

In summary, we tried to improve the activity of Ni-loaded $K_4Nb_6O_{17}$ photocatalyst for an overall water splitting by the addition of a third component, but no significant enhancement was observed for most cases. The exception was the addition of alkaline hydroxide (KOH, NaOH) into the aqueous impregnation solution. At the optimum of KOH addition, the rate of H_2 and O_2 evolution increased by ca. 1.5 times comparing to that without addition, and the quantum efficiency was 5.3% at 330 nm.

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