Photocatalytic Reaction on Layered Cs-Nb-Ti Complex Oxide

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Synopsis. Ion-exchangeable layered titano-niobates, $CsNbTi_2O_7$ and $CsNbTiO_5$, were prepared and the photocatalytic properties of those oxides as well as of the H^+-exchanged forms were investigated. H_2 or O_2 evolution reaction from an aqueous methanol solution or from an aqueous silver nitrate solution was carried out under a high pressure mercury lamp irradiation. For H_2 evolution, Pt (0.1 wt%)-loaded H^+-exchanged forms showed remarkable activity both for $CsNbTi_2O_7$ and $CsNbTiO_5$, while higher rates of O_2 evolution were obtained for H^+-exchanged forms than those for the original forms.

Using various metal oxides, many photocatalytic reactions such as H_2 and O_2 evolutions from various aqueous solutions were reported. Recently the authors reported that some ion-exchangeable layered niobates[1] and titanates[2] show a noticeable photocatalytic behavior which is distinguished from that of bulk-solid type photocatalysts such as TiO_2 and $SrTiO_3$. Especially, $A_4Nb_6O_{17}$ (A=K or Rb) was found to decompose water into H_2 and O_2 with a high and stable activity.[1,3] In this note, we report a photocatalytic behavior of niobatotitanates, i.e. $CsNbTi_2O_7$ and $CsNbTiO_5$.

Both niobatotitanates are orthorhombic, and $[(NbTi_2)O_7]^-$ layers and $[(NbTi)O_5]^-$ layers are held by cesium ions at the interlayer spaces. Cs^+ ions can be easily exchanged to other cations. Catalysts were prepared according to the previously reported papers.[4,5] $CsNbTi_2O_7$ was synthesized from Cs_2CO_3, TiO_2, and Nb_2O_5 in a molar ratio of 1.1:4:1. The mixture was first slowly heated from 673 to 1023 K, then fired at 1223 K for 4 h in a platinum crucible, and annealed at 1373 K for 2 h. The prepared catalyst had the same X-ray diffraction pattern as data in the reference.[4] When $CsNbTiO_5$ was synthesized, Cs_2CO_3, TiO_2, and Nb_2O_5 in a molar ratio of 1.1:2:1 were mixed and slowly heated from 723 to 923 K, then fired at 1023 K for 2 h in a platinum crucible.[5] The prepared catalyst has almost the same *c*-axis length as the reference data.[4,5]

H^+-exchanged catalysts were respectively prepared as follows:[6,7] 2 g of the original catalyst was stirred in 300 ml of 3 M (M=mol dm^{-3}) aqueous H_2SO_4 solution at room temperature. It took a week for $CsNbTi_2O_7$ and 3 days for $CsNbTiO_5$ to complete the substitution of H^+ ions for Cs^+ ions. After filtration the catalyst was washed with distilled water and dried at room temperature. In both cases about 100% of Cs^+ ions were found to be exchanged by H^+ ions which were examined by atomic absorption analysis.

Photocatalytic reaction was carried out in a Pyrex reactor (541 ml) connected to a closed gas circulation system. The catalyst (1 g) was suspended in an aqueous solution by magnetic stirring. Before reaction, the system was evacuated and degassed completely, and then Ar of ca. 100 Torr (1 Torr≈133.322 Pa) was introduced. The reactor was illuminated by a high pressure mercury lamp (450 W). Gas chromatography equipped directly to the gas circulation system was used for quantitative analysis of H_2 and O_2.

A mixture of CH_3OH (10 ml) and H_2O (340 ml) was used for H_2 evolution reaction, and an aqueous silver nitrate solution (1.7×10^{-2} M, 350 ml) for O_2 evolution reaction. Pt loading was carried out by a photodeposition method,[8] i.e. the addition of H_2PtCl_6 into an aqueous methanol solution before irradiation.

In Figs. 1 and 2, UV reflectance spctra of $CsNbTi_2O_7$ and $CsNbTiO_5$ as well as of those H^+-exchanged forms are shown. The band gaps estimated from those spectra, i.e. extraporating the absorption edge as shown in Figures, are summarized in Table 1. H^+-exchanged forms have smaller band gaps than the originals. The flat-band potentials determined by a slurry electrode method are also shown in Table 1. Flat-band potentials were measured by open-circuit photopotentials. At the highest light intensity there was a saturation of the potential. Under that condition the potentials was regarded to be equal to the flat-band potentials.[9] When the ion-exchange was carried out,

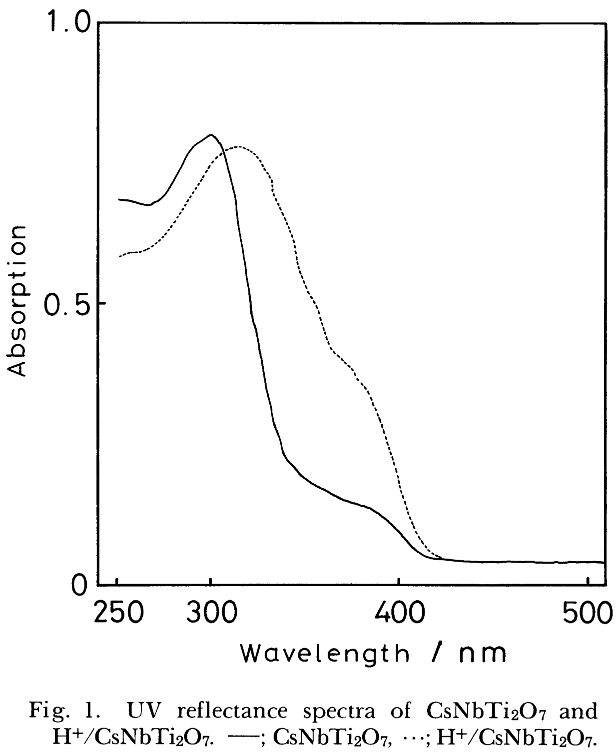

Fig. 1. UV reflectance spectra of $CsNbTi_2O_7$ and $H^+/CsNbTi_2O_7$. —; $CsNbTi_2O_7$, ···; $H^+/CsNbTi_2O_7$.

Table 1. Several Physical Properties of the Catalyst

Catalyst	Flat-band potential/eV vs. SCE	Band gap/eV	c-Axis length/nm
$CsNbTi_2O_7$	−0.56 (pH 10)	3.56	1.84
$H^+/CsNbTi_2O_7$	−0.68 (pH 3)	3.03	2.12
$CsNbTiO_5$	−0.30 (pH 11)	3.51	1.98
$H^+/CsNbTiO_5$	−0.33 (pH 3)	3.24	1.67

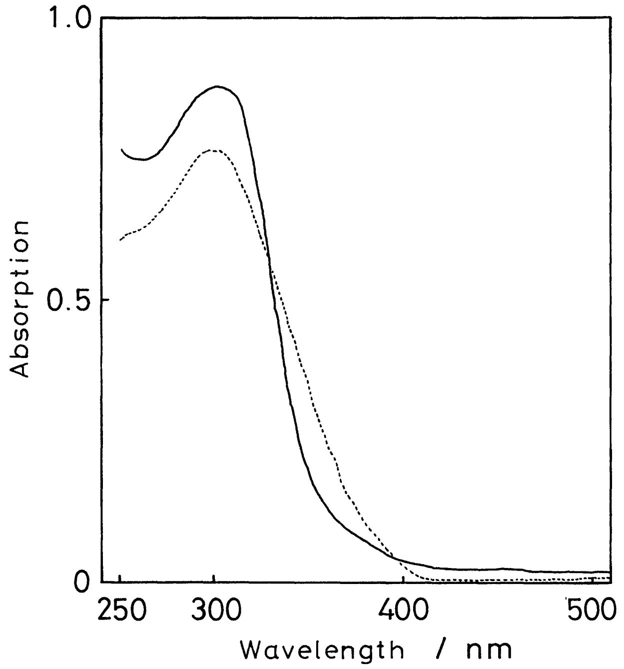

Fig. 2. UV reflectance spectra of $CsNbTiO_5$ and $H^+/CsNbTiO_5$. —; $CsNbTiO_5$ ···; $H^+/CsNbTiO_5$.

Table 2. Photocatalytic Activity of $CsNbTi_2O_7$/μmol h^{-1}

Catalyst	H_2[a]	O_2[b]
$CsNbTi_2O_7$	4.6	19
Pt-$CsNbTi_2O_7$[c]	8.5	—[d]
$H^+/CsNbTi_2O_7$	1.9	51
Pt-$H^+/CsNbTi_2O_7$[c]	87	—[d]

a) H_2 evolution reaction from a mixture of CH_3OH (10 ml) and H_2O (340 ml). b) O_2 evolution reaction from an aqueous silver nitrate solution (1.7×10^{-2} M, 350 ml). c) Pt-loaded 0.1 wt% against catalyst. d) Not measured.

Table 3. Photocatalytic Activity of $CsNbTiO_5$/μmol h^{-1}

Catalyst	H_2[a]	O_2[b]
$CsNbTiO_5$	15	1.2
Pt-$CsNbTiO_5$[c]	12	—[d]
$H^+/CsNbTiO_5$	13	24
Pt-$H^+/CsNbTiO_5$[c]	320	—[d]

a) H_2 evolution reaction from a mixture of CH_3OH (10 ml) and H_2O (340 ml). b) O_2 evolution reaction from an aqueous silver nitrate solution (1.7×10^{-2} M, 350 ml). c) Pt-loaded 0.1 wt% against catalyst. d) Not measured.

c-axis length changed in each case. If only the ion exchange from Cs^+ to H^+ ions at the interlayer spaces occurs, the interlayer spacing distance will decrease. In the case of $CsNbTi_2O_7$, the distance increased due to the hydration of the interlayer spaces,[6] while $CsNbTiO_5$ was turned into $HNbTiO_5$ without hydration, so the distance of interlayer decreased.[7]

The experimental results of H_2 evolution from an aqueous methanol solution and O_2 evolution from an aqueous silver nitrate solution are summarized in Tables 2 and 3. The rates are the values at steady state reaction condition. For the H_2 evolution reaction, both the original forms of $CsNbTi_2O_7$ and $CsNbTiO_5$ with or without Pt loading showed rather low activity. For the H^+-exchanged forms, however, the H_2 evolution rate was markedly enhanced by Pt loading while it was still low without Pt loading. In the cases of layered niobates and titanates,[2] the H_2 evolution rate from methanol aqueous solution increased dramatically with H^+-exchange not loading or Pt. To the contrary, niobatotitanates require both H^+-exchange and Pt loading treatments for the enhancement of H_2 evolution activity. At present, it is not clear the reason for the different behavior among these layered compounds. For O_2 evolution, the rates were enhanced by the H^+-exchange treatment in both cases.

In summary, photocatalytic reactions on the ion-exchangeable layered titanoniobate compounds, $CsNbTi_2O_7$ and $CsNbTiO_5$ are examined for the first time on the ion-exchangeable layered titanoniobate compounds, $CsNbTi_2O_7$ and $CsNbTiO_5$, and it was found that the H^+-exchanged forms of those compounds work as efficient photocatalysts under a high pressure mercury lamp irradiation.

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