Photocatalytic Water Splitting into H_2 and O_2 over $K_2LnTa_5O_{15}$ Powder

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$K_2LnTa_5O_{15}$ (Ln=La, Pr, Nd, Sm, Gd, Tb, Dy, and Tm) loaded with NiO co-catalysts showed photocatalytic activities for water splitting into H_2 and O_2 in stoichiometric amounts under UV light irradiation ($h\nu$ > 3.9-4.1 eV). The photocatalytic activities strongly depended on the lanthanide ions. Among them, $K_2PrTa_5O_{15}$ and $K_2SmTa_5O_{15}$ showed relatively high activities.

Development of new photocatalysts for water splitting is an important theme. Most photocatalysts reported for the water splitting are titanates.[1,2] Authors have studied tantalate photocatalysts as a new series of photocatalyst materials and have reported that NiO-loaded $K_3Ta_3Si_2O_{13}$, $NaTaO_3$, $SrTa_2O_6$, $BaTa_2O_6$, and $Sr_2Ta_2O_7$ showed high activities for the water splitting.[3–7] On the other hand, Ishihara et al. have found that Ti, Zr, and Hf-doped $KTaO_3$ showed high activities.[8,9] Machida and co-workers have reported photocatalytic activities of $RbLnTa_2O_7$ with a layered perovskite structure.[10,11] These photoactive tantalates possess the framework of TaO_6 octahedra sharing corners as seen in a perovskite structure. Excited energy becomes delocalized as the bond angle of M–O–M is getting close to 180°.[12] The increase in the degree of delocalization indicates the increase in the probability that photogenerated electron-hole pairs reach active sites for H_2 or O_2 evolution on the surface. Corner-sharing of MO_6 octahedra leads the bond angle of M–O–M to be close to 180°. Therefore, the corner-shared structure seems to play an important role for photocatalytic properties. It is important to study the photocatalytic behavior of materials with the corner-shared structure other than perovskite. $K_2LnTa_5O_{15}$ consists of a tungsten bronze structure in which TaO_6 octahedra are corner-shared each other as shown in Figure 1.[13] From this structure, photocatalytic properties of $K_2LnTa_5O_{15}$ are of interest. This paper reports photocatalytic water splitting into H_2 and O_2 over the $K_2LnTa_5O_{15}$ powder.

$K_2LnTa_5O_{15}$ powders were prepared by solid state reactions. Starting materials used were as follows; K_2CO_3 (Kanto Chemical, purity; 99.5%), La_2O_3 (Wako Pure Chemical, purity; 99.99%), $Ce_2(CO_3)_3{\cdot}8H_2O$ (Wako Pure Chemical, purity; 98%), Pr_6O_{11} (Wako Pure Chemical, purity; 99.5%), Nd_2O_3 (Rare Metallic, purity; 99.99%), Sm_2O_3 (Wako Pure Chemical, purity; 99.9%), Eu_2O_3 (Shin-etsu Chemical, purity; 99.9%), Gd_2O_3 (Kanto Chemical, purity; 99.95%), Tb_4O_7 (Soekawa Chemical, purity; 99.5%), Dy_2O_3 (Shin-etsu Chemical, purity; 99.9%), Tm_2O_3 (Soekawa Chemical, purity; 99.9%), Yb_2O_3 (Wako Pure Chemical, purity; 99.9%), Ta_2O_5 (Rare Metallic, purity; 99.99%). Each mixtures of K_2CO_3 (10% excess), lanthanide oxide, and Ta_2O_5 was calcined at 1620 K for 10 h in air using a platinum crucible.[13] The products were confirmed to be single phases by X-ray diffraction (Rigaku, RINT-1400). NiO co-catalysts were loaded on the $K_2LnTa_5O_{15}$ powder by an impregnation method from $Ni(NO_3)_2$. The NiO/$K_2LnTa_5O_{15}$ powders were calcined at 620 K for 1 h in air. Photocatalytic water splitting was carried out in a gas-closed circulation system. Photocatalyst powder (1 g) was dispersed in 350 mL of pure water in an inner irradiation quartz cell by a magnetic stirrer. Samples were irradiated with a 400 W high pressure mercury lamp (SEN, HL400EH-5). Amounts of evolved H_2 and O_2 were determined using a gas chromatography (Shimadzu, GC-8A). Diffuse reflectance spectra were measured using a UV-VIS-NIR spectrometer with an integrating sphere (JASCO, Ubest-570). The diffuse reflectance spectra were converted by the Kubelka-Munk method.

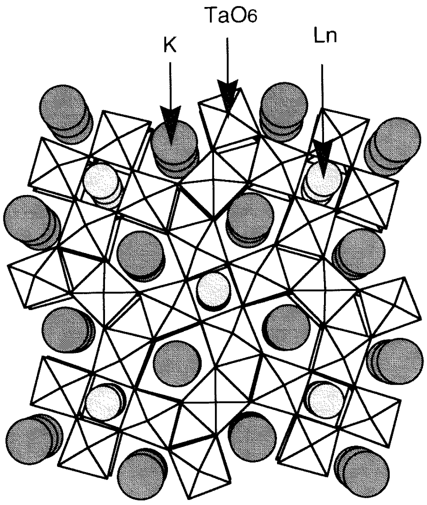

Figure 1. Tungsten bronze structure of $K_2LnTa_5O_{15}$.[13]

Figure 2 shows diffuse reflectance spectra of some $K_2LnTa_5O_{15}$. The onset of the spectrum of $K_2PrTa_5O_{15}$ was in the position at longer wavelength and that of $K_2SmTa_5O_{15}$ was at shorter wavelength than that of $K_2LaTa_5O_{15}$. The onsets of $K_2LnTa_5O_{15}$ (Ln=Nd, Gd, Dy, Tm, and Yb) were in similar positions to that of $K_2SmTa_5O_{15}$ while $K_2TbTa_5O_{15}$ was similar to $K_2PrTa_5O_{15}$. These shifts indicate that rare earth ions affect the band structure of the framework consisting of TaO_6. The different ionic radius leads the different degree of distortion of the TaO_6 framework. Polarizing power electrostatically influences the orbitals of the TaO_6 framework. Therefore, the energy structure of the TaO_6 framework is changed by these factors, resulting in the shift of the onset. 4d and 4f orbitals of rare earth ions might also affect the energy state of the TaO_6 framework or form some energy levels in the band structure as indicated by Machida et al.[10,11]

Table 1 shows photocatalytic activities for water splitting over NiO-loaded $K_2LnTa_5O_{15}$. $K_2PrTa_5O_{15}$ and $K_2SmTa_5O_{15}$ showed high activities whereas activities of $K_2CeTa_5O_{15}$,

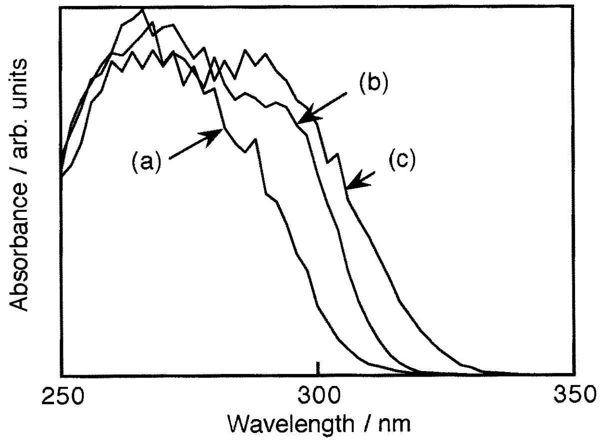

Figure 2. Diffuse reflectance spectra of (a) $K_2SmTa_5O_{15}$, (b) $K_2LaTa_5O_{15}$, and (c) $K_2PrTa_5O_{15}$.

$K_2EuTa_5O_{15}$, and $K_2YbTa_5O_{15}$ were negligible. Because europium and ytterbium can take a divalent oxidation number relatively easily, they may work as electron trapping sites, resulting in the decrease in the photocatalytic activities. Although $K_2CeTa_5O_{15}$ absorbed visible light the activity was very low. The order of the photocatalytic activity to the kind of rare earth ions for $K_2LnTa_5O_{15}$ was different from that for $RbLnTa_2O_7$ with layered perovskite structure (Nd>Sm>>La>Pr) reported by Machida et al.[10,11] The difference in the order indicates that effects of rare earth ions to the band structure of the TaO_6 framework depend on the crystal structure.

Table 1. Photocatalytic water splitting over NiO(0.5 wt%)/$K_2LnTa_5O_{15}$ powder

Catalyst	Band gap / eV	Amounts of gases evolved/ µmol[a] H_2	O_2
$K_2LaTa_5O_{15}$	4.0	175	74
$K_2CeTa_5O_{15}$	2.5	5	3
$K_2PrTa_5O_{15}$	3.8	517	238
$K_2NdTa_5O_{15}$	4.1	125	60
$K_2SmTa_5O_{15}$	4.1	623	272
$K_2EuTa_5O_{15}$	3.9	2	0
$K_2GdTa_5O_{15}$	4.1	240	73
$K_2TbTa_5O_{15}$	3.9	174	77
$K_2DyTa_5O_{15}$	4.1	358	172
$K_2TmTa_5O_{15}$	4.1	173	70
$K_2YbTa_5O_{15}$	4.1	7	1

[a] After 5 hours. Photocatalyst; 1.0 g, water; 350 ml, reaction cell; inner irradiation-type reaction cell made of quartz, light source; high pressure mercury lamp (400 W).

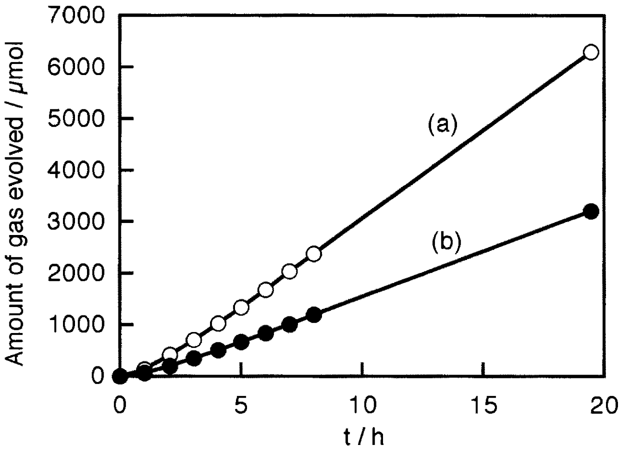

Figure 3. Photocatalytic decomposition of pure water over nontreated NiO(0.1wt%)/$K_2PrTa_5O_{15}$. (a): H_2, (b): O_2

Figure 3 shows time courses of H_2 and O_2 evolution by water splitting on NiO(0.1 wt%)/$K_2PrTa_5O_{15}$. H_2 (334 µmol/h) and O_2 (170 µmol/h) steadily evolved in stoichiometric amounts. The turn over numbers of the amount of reacted electrons to the total number of tantalum and to the total number of nickel loaded were 3.4 and 940 at 20 h of the reaction time, respectively. These turn over numbers indicate that the reaction proceeded photocatalytically.

In conclusion, $K_2LnTa_5O_{15}$ with a tungsten bronze structure consisting of the framework of TaO_6 shared corners has arisen as a new photocatalyst group for water splitting into H_2 and O_2. This result suggests the importance of the corner-shared structure on photocatalyst materials.

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References

1 A. Kudo, *Hyomen (Surface)*, **36**, 625 (1998).
2 K. Domen, J.N. Kondo, M. Hara, and T. Takata, *Bull. Chem. Soc. Jpn.*, **73**, 1307 (2000).
3 A. Kudo and H. Kato, *Chem. Lett.*, **1997**, 867.
4 H. Kato and A. Kudo, *Chem. Phys. Lett.*, **295**, 487 (1998).
5 H. Kato and A. Kudo, *Catal. Lett.*, **58**, 153 (1999).
6 H. Kato and A. Kudo, *Chem. Lett.*, **1999**, 1207.
7 A. Kudo, H. Kato, and S. Nakagawa, *J. Phys. Chem. B*, **104**, 571 (2000).
8 T. Ishihara, H. Nishiguchi, K. Fukamachi, and Y. Takita, *J. Phys. Chem. B*, **103**, 1 (1999).
9 C. Mitsui, H. Nishiguchi, K. Fukamachi, T. Ishihara, and Y. Takita, *Chem. Lett.*, **1999**, 1327.
10 M. Machida, J. Yabunaka, and T. Kijima, *Chem. Commun.*, **1999**, 1939.
11 M. Machida, J. Yabunaka, and T. Kijima, *Chem. Mater.*, **12**, 812 (2000).
12 G. Blasse, *J. Solid State Chem.*, **72**, 72 (1988).
13 F. Brik, R. Enjalbert, C. Roucau, and J . Galy, *J. Solid State Chem.*, **122**, 7 (1996).