Photocatalytic Decomposition of Pure Water into H_2 and O_2 over $SrTa_2O_6$ Prepared by a Flux Method

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Orthorhombic (orth.) $SrTa_2O_6$ powder which was hardly obtained by a solid state reaction was easily synthesized by using a strontium borate flux. The native $SrTa_2O_6$ powder showed photoluminescence and a photocatalytic activity for decomposition of pure water into H_2 and O_2. The photocatalytic activity was drastically increased by loading a NiO co-catalyst even without pretreatment. The optimum amount of NiO loaded was 0.10 wt%. The quantum yield of the NiO(0.10 wt%)/$SrTa_2O_6$ photocatalyst was 7% at least.

The photocatalytic decomposition of water has been studied from a viewpoint of photon energy conversion. Some oxides consisting of d^0 metal ions in groups 4 and 5 can decompose water into H_2 and O_2 in a stoichiomtric ratio under UV irradiation.[1-8] Among their photocatalysts, the authors have reported that metal tantalate is a new group of photocatalysts for the water decomposition.[4-6] For example, a NiO/$NaTaO_3$ photocatalyst gave 28% of a quantum yield for the water decomposition at 270 nm.[6] Moreover, $BaTa_2O_6$ also showed a high activity.[5] These results have attracted the authors to investigate the photocatalytic activities of other alkaline earth tantalates. In the previous paper,[5] however, $SrTa_2O_6$ had not been obtained by a solid state reaction at 1470–1700 K. In the present paper, the easy preparation of orth. $SrTa_2O_6$ powder by using a SrB_2O_4 flux and the photocatalytic activity for the water decomposition over the $SrTa_2O_6$ powder are reported.

Orth. $SrTa_2O_6$ powder was synthesized by calcining a mixture of $SrCO_3$ (Kanto Chemicals; 96.0%), Ta_2O_5 (Rare Metallic; 99.99%), and H_3BO_3 (Kanto Chemicals; 99.0%) in the mole ratio of 1.0:0.9:0.2 at 1370 K for 10 h in air using a platinum crucible. The boric acid was added in the starting materials to form a SrB_2O_4 flux. The SrB_2O_4 flux was removed from the product by washing with distilled water before use. $CaTa_2O_6$ powder was synthesized by a conventional solid state reaction from the starting materials of $CaCO_3$ (Kanto Chemicals; 96.0%) and Ta_2O_5 at 1450 K for 120 h. The prepared materials were confirmed by X-ray diffraction (Rigaku; RINT-1400). NiO co-catalysts were loaded by an impregnation method from an aqueous $Ni(NO_3)_2$ solution. The NiO-loaded photocatalysts were calcined at 640 K for 1 h in air.

Measurements of photophysical properties and photocatalytic reactions were carried out as described in a previous paper.[6] A surface area was determined by BET measurement (Coulter; SA3100). The orth. $SrTa_2O_6$ particles were observed by a scanning electron microscope (Hitachi; S-5000).

Figure 1 shows XRD patterns of $SrTa_2O_6$ powder prepared by a flux method and solid state reactions. A single phase of orth. $SrTa_2O_6$ powder was obtained by the flux method at 1370K for 10 h while the mixture of $Sr_2Ta_2O_7$ and $SrTa_4O_{11}$ was formed by the solid state reaction at 1700 K for 48 h. On the other hand, in the product by the solid state reaction at 1470 K for 10 h, the starting materials and impurity phases were obtained in addition to $SrTa_2O_6$. Squarish particles were observed by SEM as shown in Figure 2. The particle sizes of $SrTa_2O_6$ prepared by the flux method were 2-12 nm. The specific surface area was 0.6 m^2g^{-1}. The sharp diffraction profile and SEM observation suggest that the $SrTa_2O_6$ powder was well-crystallized in spite of calcination at low temperature.

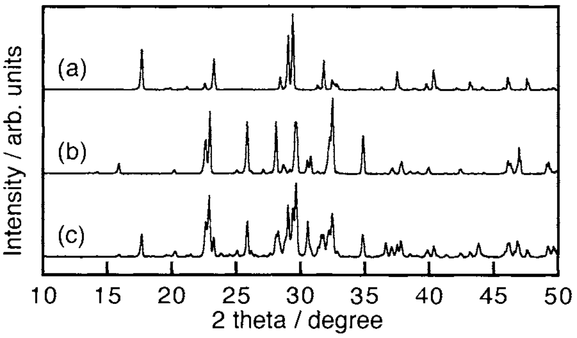

Figure 1. XRD patterns of $SrTa_2O_6$ prepared by (a) a flux method at 1370 K for 10 h, and solid state reactions (b) at 1700 K for 48 h and (c) at 1470 K for 10h.

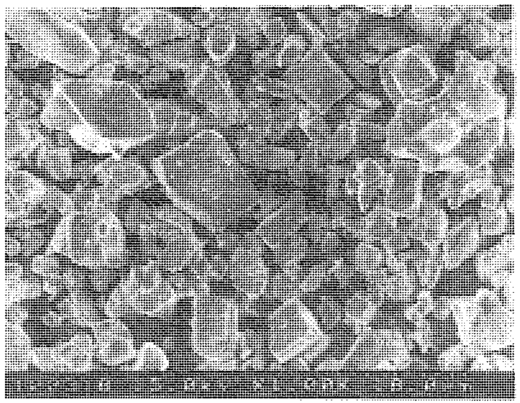

Figure 2. SEM photograph of orth. $SrTa_2O_6$ prepared by a flux method.

Figure 3 shows a diffuse reflectance spectrum at room temperature and photoluminescence spectra at 77 K of orth. $SrTa_2O_6$. The band gap was estimated to be 4.4 eV from the onset of the diffuse reflectance spectrum (281 nm). Orth. $SrTa_2O_6$ showed the broad emission around 405 nm by photoexcitation at 255 nm.

The decomposition of pure water over $SrTa_2O_6$ photocatalysts is shown in Figure 4. The $SrTa_2O_6$ photocatalyst steadily decomposed water into H_2 and O_2 without any co-catalysts such as Pt and NiO. The rates of H_2 and O_2 evolution were 140 and 66 μmol h^{-1}, respectively. The photocatalytic activity of $SrTa_2O_6$ was drastically increased by loading NiO without the

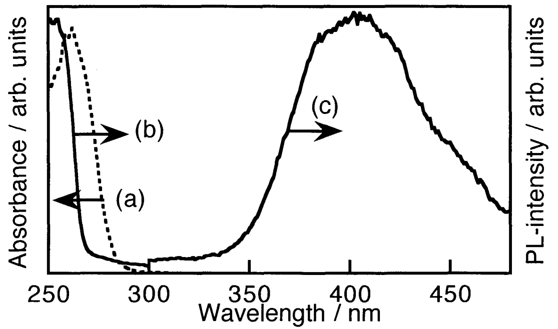

Figure 3. (a) Diffuse reflectance spectrum at 300 K, and (b) excitation and (c) emission spectra at 77 K of orth. $SrTa_2O_6$.

activation pretreatment, being similar to other tantalate photocatalysts.[4-6] The maximum activity (H_2: 960 μmol h^{-1}, O_2: 490 μmol h^{-1}) was obtained when 0.10 wt% of NiO was loaded. The quantum yield of the NiO(0.10 wt%)/$SrTa_2O_6$ photocatalyst was 7% at 270 nm at least. NiO loaded works as an active site for the H_2 evolution.[9] On the other hand, the excess amount of NiO unnecessarily covers the surface of $SrTa_2O_6$ and shields incident light. The balance of the positive and negative effects at 0.10 wt% caused the maximum activity as discussed in a previous paper.[6]

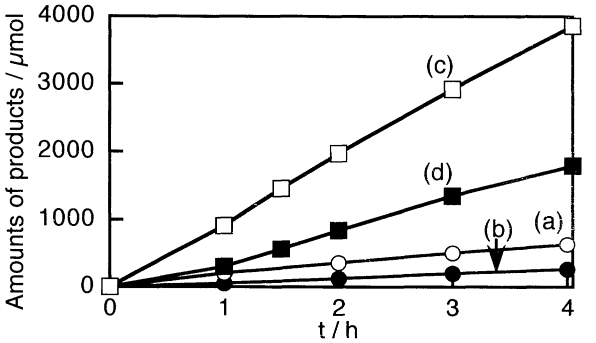

Figure 4. Photocatalytic decomposition of pure water over $SrTa_2O_6$ ((a): H_2, (b): O_2), and nontreated NiO(0.10 wt%)/$SrTa_2O_6$ ((c): H_2, (d): O_2) photocatalysts.

Orth. $CaTa_2O_6$ which possesses the similar structure to orth. $SrTa_2O_6$[10] also showed the activity for the water decomposition. However, the activity of $CaTa_2O_6$ (H_2: 21 μmol h^{-1}, O_2: 8.3 μmol h^{-1}) was lower than that of $SrTa_2O_6$. The activity of the $CaTa_2O_6$ photocatalyst was also increased by the NiO-loading without the pretreatment (H_2: 72 μmol h^{-1}, O_2: 32 μmol h^{-1}).

The photocatalytic activities of orth. ATa_2O_6 (A = Ca, Sr, Ba) are summarized in Table 1. The present study revealed that the order of the activities of ATa_2O_6 photocatalysts was $SrTa_2O_6$ > $BaTa_2O_6$ > $CaTa_2O_6$. Two factors affecting the photocatalytic activities can be considered. The order of the band gap of ATa_2O_6 is $SrTa_2O_6$ > $BaTa_2O_6$ > $CaTa_2O_6$. The valence bands of these photocatalysts are formed by 2p orbitals of O^{2-}. These facts indicate that the conduction band level of $SrTa_2O_6$ is more negative than those of $BaTa_2O_6$ and $CaTa_2O_6$, suggesting that the potential of excited electrons for water reduction to form H_2 in $SrTa_2O_6$ is higher than those of $BaTa_2O_6$ and $CaTa_2O_6$. Therefore, the water decomposition proceeds more easily over $SrTa_2O_6$ than $BaTa_2O_6$ and $CaTa_2O_6$. On the other hand, the correlation between the photocatalytic activity and the emission wavelength has been observed in the case of three different crystal phases of $BaTa_2O_6$.[5] In the photoluminescence, $SrTa_2O_6$ gave an emission band at the shortest wavelength among ATa_2O_6, indicating the presence of the largest transferring excitation energy in $SrTa_2O_6$. Thus, the difference in the photocatalytic activity among ATa_2O_6 seems to be due to the conduction band level and the magnitude of transferring excitation energy.

Table 1. Photoluminescence properties and photocatalytic activities of alkaline earth tantalates

Catalyst	Band gap / eV	Emission max.[a] / nm	Activity / μmol h^{-1}	
			H_2	O_2
$CaTa_2O_6$[b]	4.0	473	72	32
$SrTa_2O_6$[b]	4.4	405	960	490
$BaTa_2O_6$[c]	4.1	460	629[d]	303[d]

Catalyst; 1 g, H_2O; 390 ml, light source; 400W High pressure mercury lamp, reaction cell; inner irradiation cell made of quartz. [a] Observed at 77 K. [b] 0.1 wt%, [c] 0.3 wt% of NiO were loaded. [d] Ref. 5.

In conclusion, NiO/$SrTa_2O_6$ prepared by a flux method has arisen as a highly active photocatalyst for the decomposition of pure water under UV irradiation.

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