Photocatalytic Performance of $Ba_5Ta_4O_{15}$ to Decomposition of H_2O into H_2 and O_2

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The photocatalytic performance of barium tantalates in the decomposition of H_2O into H_2 and O_2 was investigated. $Ba_5Ta_4O_{15}$ that was prepared under Ta rich atmosphere exhibited remarkable photocatalytic activity. Under the same reaction conditions, its activity was the highest among all of the alkali earth-tantalum mixed-oxide photocatalysts prepared.

Photocatalysts, which directly convert photon energy to chemical energy, have been widely studied for decomposition of H_2O into H_2 and O_2. A series of mixed oxides containing the Ta^{5+} ion are known to show high photocatalytic performance in this decomposition reaction.[1–4] In particular, La^{3+} and alkali earth ions-doped $NaTaO_3$ exhibited excellent activity.[5–7] On the other hand, alkali earth-tantalates, particularly $Sr_2Ta_2O_7$ with a layered perovskite structure, have also been reported to be an active photocatalyst for H_2O decomposition.[8] Despite this, systematic investigations have not yet been performed on Ba^{2+}-containing mixed oxides.

An investigation has been carried out on the photocatalytic properties of Ba^{2+}-containing mixed oxides for the decomposition of H_2O. The photocatalytic performance of the characteristic barium–tantalum mixed oxide, $Ba_5Ta_4O_{15}$, and other related mixed oxides is reported.

The photocatalysts used in the present work were prepared by a complex-polymerization method.[9,10] The precursor of the mixed oxide, which was obtained by the calcination of polymer-complex at 873 K, was subsequently calcined at different temperatures. The prepared mixed oxides were characterized by XRD and UV–vis diffuse reflectance spectroscopy. NiO was used as a co-catalyst and these NiO-supported photocatalysts were prepared by a conventional impregnation method. Photocatalytic reaction was carried out in an inner irradiation type photoreaction vessel made of quartz connected with closed gas circulation system (the dead volume is 430 mL). The photocatalyst (1 g) was suspended in well degassed water in the vessel. A high-pressure mercury lamp (450 W, USHIO UM-452) supplied the irradiation. Evolved gases were analyzed by gas chromatograph.

The $Ba_5Ta_4O_{15}$ photocatalysts used in this work were prepared from the two kinds of precursor. One contained Ba and Ta ion in the stoichiometric amount of $Ba_5Ta_4O_{15}$ (BaTa54-A) and the other contained the excess amount of Ta ion (25 atom % excess) compared with the stoichiometry (BaTa54-B), so that the amount of Ba and Ta ions was the same. Both of the photocatalysts were prepared by the calcination of the precursor at several different temperatures.

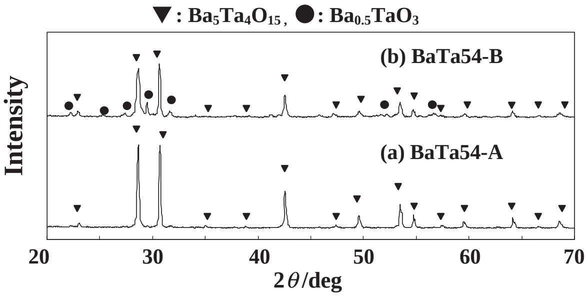

Figure 1. XRD pattern of (a) BaTa54-A and (b) BaTa54-B.

Figure 1 shows the XRD pattern of (a) BaTa54-A and (b) BaTa54-B. Both of the photocatalysts were prepared by calcining the precursors at 1273 K. As shown in Figure 1a, the XRD pattern is in good agreement with the pattern of $Ba_5Ta_4O_{15}$. This means that the BaTa54-A is the single phase of $Ba_5Ta_4O_{15}$. On the other hands, the XRD pattern of BaTa54-B, as shown in Figure 1b, mainly consists of the pattern of $Ba_5Ta_4O_{15}$, but various other diffraction peaks can be observed. These peaks match with the diffraction pattern of $Ba_{0.5}TaO_3$. Therefore, BaTa54-B is a mixture of $Ba_5Ta_4O_{15}$ and $Ba_{0.5}TaO_3$, but still mainly consists of $Ba_5Ta_4O_{15}$. It is noticed in Figure 1 that the shapes of the diffract pattern attributed to $Ba_5Ta_4O_{15}$ in BaTa54-A and B are different, such as the intensity ratio of the peaks at 28.8 degree and 30.9 degree. This difference probably originates from the different morphology of $Ba_5Ta_4O_{15}$ crystal in the photocatalysts. From the results of UV diffuse reflectance spectra, a strong absorption band, originating from the band gap excitation, was observed at a wavelength shorter than 320 nm in both of the photocatalysts. The band gap energy can be estimated to be 3.9 eV from the absorption edge of the spectrum.

The progress of the photocatalytic decomposition of H_2O over NiO (0.2 wt %) supported BaTa54-A and BaTa54-B is shown in Figure 2. Both H_2 and O_2 are produced in the stoichiometric amounts simultaneously from the beginning of the irradiation over both of the photocatalysts. In the first run, the photocatalytic reaction was monitored for 3 h after which the irradiation was stopped. The gas phase was evacuated, and the reaction cell was kept in the dark for 1 h to confirm the absence of any further H_2 and O_2 without irradiation. Irradiation was started again for the second run. The constant evolution of H_2 and O_2 was also observed in the second run. Noticeably, the activity of BaTa54-B is much higher than that of BaTa54-A and the activity improved in the second run. The pressure in the system reached 1 atmosphere already after 2.5 h when using BaTa54-B a photocatalyst. These results suggest that $Ba_5Ta_4O_{15}$ is an effective photocatalyst for the decomposition of H_2O, and a mixture with $Ba_{0.5}TaO_3$ prepared under a Ta^{5+} rich atmosphere

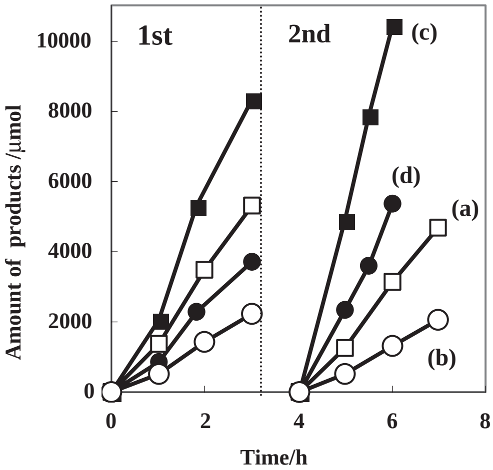

Figure 2. Evolution of H_2 and O_2 in time during photocatalytic decomposition of H_2O over NiO(0.2 wt %)/BaTa54-A ((a): H_2, (b): O_2), and BaTa54-B ((c): H_2, (d): O_2).

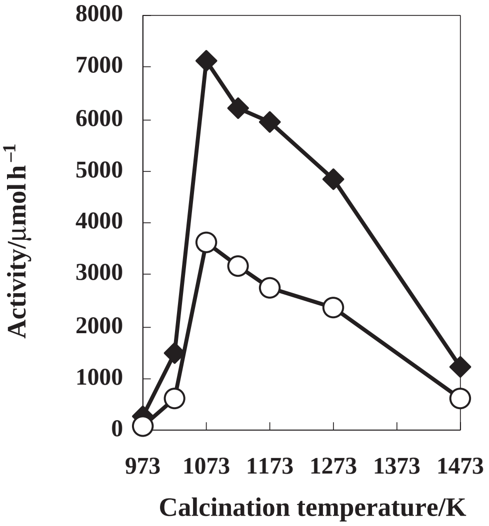

Figure 3. Effects of the calcination temperature on the photocatalytic activity of H_2O decomposition into H_2 and O_2 over NiO(0.2 wt %)/BaTa54-B; closed square: H_2, open circle: O_2.

positively acted to improve the photocatalytic activity. The positive effect is probably originated with the morphology of $Ba_5Ta_4O_{15}$ crystal in BaTa54-B.

Figure 3 shows the effect of calcination temperatures of the catalyst precursor of BaTa54-B on the photocatalytic activity of H_2O decomposition. The photocatalytic activity is dependent on the calcination temperature and the photocatalyst calcined at 1073 K showed the maximum activity of 7.1 mmol/h for H_2 and 3.6 mmol/h for O_2. However, the activity decreased by further calcination above 1073 K. The XRD measurement revealed that more $Ba_{0.5}TaO_3$ in photocatalysts calcined below 973 K, and $Ba_5Ta_4O_{15}$ was mainly observed in the photocatalysts calcined above 1073 K. This suggests that the $Ba_5Ta_4O_{15}$ phase is important for producing the photocatalytic activity. The diffraction peaks became sharp at higher temperature. This means that the crystallization of the photocatalyst was proceeding. The decrease in photocatalytic activity at the calcination temperatures higher than 1073 K is probably caused by changing the morphology of the photocatalyst originated from the crystal growth although further detailed examination is necessary.

Table 1. Photocatalytic activity of various alkali earth-tantalates in H_2O decomposition

Catalysts	Amount of NiO loaded (wt %)	Activity/μmol h	
		H_2	O_2
BaTa54-A	none	25.86	7.17
BaTa54-A	0.20	2076	907
BaTa54-B	none	83.75	37.70
BaTa54-B	0.20	7110	3621
$BaTa_2O_6$	0.20	451	185
$Ca_2Ta_2O_7$	0.20	524	213
$Sr_2Ta_2O_7$	0.70	1260	630

The photocatalytic activity of H_2O decomposition over various alkali earth-tantalates is listed in Table 1. The photocatalysts were prepared by the preferable condition and the activity was examined under the same experimental condition as the present work. These photocatalysts show relatively high performance to the reaction. It is obvious that the series of prepared $Ba_5Ta_4O_{15}$ exhibit remarkable performance. Particularly, BaTa54-B, the mixture of $Ba_5Ta_4O_{15}$ and $Ba_{0.5}TaO_3$, exhibited highest activity.

It is notable that the $Ba_5Ta_4O_{15}$ photocatalyst exhibited high performance in the photodecomposition of H_2O into H_2 and O_2. Furthermore, the activity can be significantly improved by controlling the preparation conditions. The detailed effect on the improvement of the photocatalytic activity is under investigation.

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