Improvement of Photocatalytic Activity of Titanate Pyrochlore $Y_2Ti_2O_7$ by Addition of Excess Y

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We found that $Y_2Ti_2O_7$ samples prepared by polymerized complex method with excess amounts (5%) of Y showed higher photocatalytic activity for overall water splitting reaction than those prepared with a stoichiometric ratio of Y and Ti (1:1). The excess Y prevented the formation of the impurity TiO_2 rutile which forms on the surface of catalysts at high temperatures and thereby decreases photocatalytic activity.

Photocatalytic water splitting into H_2 and O_2 by semiconductors has attracted much attention, because of its potential for production of clean fuel, H_2, from water utilizing solar light.[1] Various mixed oxides are reported to split water into H_2 and O_2 in the stoichiometric ratio under UV light irradiation. However, most of the active materials are perovskite-type compounds, such as $SrTiO_3$,[2–4] $K_2La_2Ti_3O_{10}$,[5] $KTaO_3$,[6] $NaTaO_3$,[7] $Sr_2M_2O_7$ (M = Nb, Ta),[8] $RbNbTa_2O_7$,[9] and $La_2Ti_2O_7$.[10] We recently reported water splitting over NiO_x-loaded $Y_2Ti_2O_7$ as the first example of an active photocatalyst with a pyrochlore-structure, a wide variety of compounds with empirical formula $A_2B_2O_7$.[11] However, the efficiencies of water splitting over the $Y_2Ti_2O_7$ photocatalyst were still low compared with those of perovskite-type compounds such as $NaTaO_3$. In this study, we report an improvement of the photocatalytic activity of $Y_2Ti_2O_7$ photocatalyst prepared by the modified polymerized complex (PC) method. We found that the addition of an excess amount of Y (5% excess to Ti) significantly improved the photocatalytic activity of $Y_2Ti_2O_7$ photocatalyst. The excess amount of Y in the preparation prevented the formation of the impurity TiO_2 rutile phase, formed at high temperature which decreases the photocatalytic activity.

Powdered $Y_2T_2O_7$ samples were prepared by the PC method.[12] First, 0.01 mol of titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$) was dissolved in 0.4 mol of ethylene glycol (EG). Subsequently, 0.3 mol of anhydrous citric acid (CA) was added to the solution with continuous stirring. After complete dissolution of the CA, 0.0105 mol (excess amount (5%) of Y to Ti) of $Y(NO_3)_3 \cdot 6H_2O$ was added. The mixture was magnetically stirred for 1 h to produce a colorless solution. The solution was heated ca. 130 °C to accelerate esterification reactions between CA and EG and precipitate a transparent glassy resin. The resin was fired in an electric furnace for 2 h at 360 °C. The resulting black solid mass was ground into a powder and calcined on a Al_2O_3 plate at 800–1200 °C for 2 h in air. The $Y_2Ti_2O_7$ samples prepared with excess amount (5%) of Y to Ti are referred to $Y_2Ti_2O_7$-e. The $Y_2Ti_2O_7$ samples prepared with a stoichiometric ratio of Y and Ti are referred to $Y_2Ti_2O_7$-s. NiO_x cocatalyst was loaded on the photocatalyst powder to promote H_2 production.[4] The photocatalytic reaction was examined using a gas closed circulation system. The photocatalyst powder (0.5 g) was suspended in distilled water (400 mL) by a magnetic stirrer in an inner-irradiation reaction cell. The light source (400 W high-pressure mercury lamp, Riko Kagaku Japan) was covered with a water jacket (quartz glass; cutoff $\lambda < 200$ nm) to keep the reactor temperature constant at 20 °C by cooling water. The gases evolved were analyzed by on-line gas chromatography (TCD, molecular sieve 5A) connected with the circulation system. Apparent quantum yield was measured using a reactor cell with a side window made of quartz and a 500-W high-pressure mercury lamp attached with a band-pass filter (Asahi Spectra Co., Ltd., MZ0313). The incident light intensity was measured with a thermopile power meter (SCIENTECH, S310).

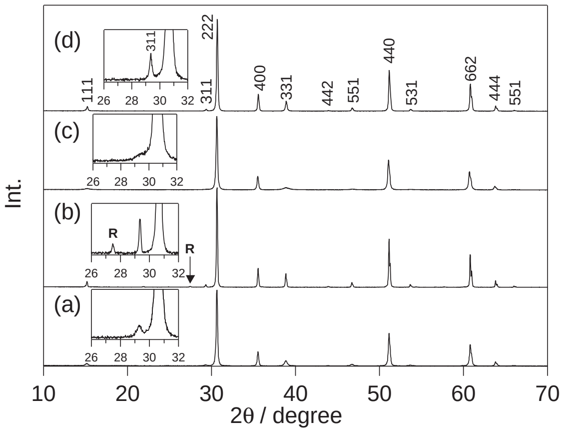

Figure 1. X-ray diffraction patterns of samples obtained by heating $Y_2Ti_2O_7$-s at (a) 800 °C, and (b) 1000 °C, and samples obtained by heating $Y_2Ti_2O_7$-e at (c) 800 °C, and (d) 1000 °C, in air for 2 h prepared by the polymerized complex method. R indicates main peak of TiO_2 rutile (110).

Figure 1 shows the X-ray diffraction (XRD) patterns of $Y_2Ti_2O_7$-s and $Y_2Ti_2O_7$-e samples prepared using the PC method followed by calcination at 800 and 1000 °C for 2 h in air. The XRD pattern of $Y_2Ti_2O_7$-s calcined at 800 °C indicated a pure pyrochlore structure, while that of $Y_2Ti_2O_7$-s calcined at 1000 °C contained impurity peaks assigned to TiO_2 rutile, as shown in Figure 1. The XRD patterns of $Y_2Ti_2O_7$-e indicate formation of a pure pyrochlore structure, regardless of calcination temperatures. No peak assigned to other impurities, such as Y_2O_3, was observed. UV–vis spectra of $Y_2Ti_2O_7$ samples calcined at 1000 °C are shown in Figure 2. The absorption edge of the $Y_2Ti_2O_7$-s was around 410 nm, similar to that of TiO_2 rutile, as shown in Figure 2. The $Y_2Ti_2O_7$-e prepared with an excess amount of Y showed the absorption edge at ca. 350 nm, agreeing with that of $Y_2Ti_2O_7$ prepared by the solid state reaction method.[13] These results indicate that the impurity TiO_2 ru-

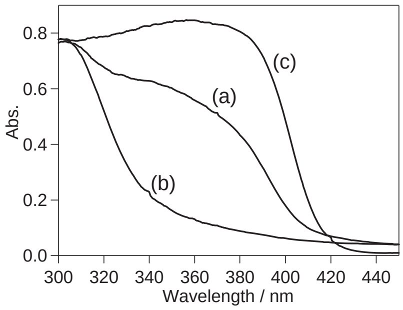

Figure 2. UV–vis spectra of (a) $Y_2Ti_2O_7$-s 1000 °C, (b) $Y_2Ti_2O_7$-e 1000 °C, and (c) TiO_2 rutile.

tile phase was formed during calcination above 1000 °C when the precursor was prepared with the stoichiometric amount of Y to Ti (1:1). The formation of TiO_2 rutile phase at high temperature was effectively prevented by the addition of excess Y in the precursor. We previously reported the band gap of $Y_2Ti_2O_7$ as 3.0 eV, but it was our mistake that results from the presence of TiO_2 rutile phase.[11]

The rates of H_2 evolution over the NiO_x (1 wt %)-$Y_2Ti_2O_7$-s and the NiO_x (1 wt %)-$Y_2Ti_2O_7$-e samples are plotted as a function of the calcination temperature in Figure 3, wherein data for specific surface areas of each sample are also shown. The rates of O_2 evolution were not shown in Figure 3 because H_2 and O_2 gases were evolved in the stoichiometric ratio (H_2:O_2 = 2:1) in all cases we examined. The rates of H_2 evolution over $Y_2Ti_2O_7$-e photocatalysts significantly increased with the increase of calcination temperature from 800 to 1000 °C, and decreased at 1200 °C. The surface areas of $Y_2Ti_2O_7$-e drastically decreased with the increase of calcination temperature from 800 to 1000 °C, indicating an increase in crystallinity. Therefore, the increase of the photocatalytic activity from 800 to 1000 °C is almost certainly due to the increase in crystallinity of the $Y_2Ti_2O_7$-e photocatalyst. The rates of H_2 evolution over $Y_2Ti_2O_7$-s photocatalysts gradually decreased with the increase of calcination temperature, in spite of the increasing crystallinity indicated by the decrease in the surface area. As shown in Figure 1, the $Y_2Ti_2O_7$-s samples calcined above 1000 °C contained the impurity phase of TiO_2 rutile. It is known that the TiO_2 rutile powder photocatalyst itself cannot split pure water into H_2 and O_2. Therefore, the formation of TiO_2 rutile possibly decreased the activity of $Y_2Ti_2O_7$-s photocatalysts calcined at high temperature. As shown in Figure 2, the $Y_2Ti_2O_7$-s samples calcined at 1000 °C showed strong absorption at wavelengths longer than 350 nm, regardless of the small amount of TiO_2 rutile phase indicated by the weak XRD peak. The impurity phases of TiO_2 rutile formed on the surface of $Y_2Ti_2O_7$-s samples and deactivated the active sites for the reaction.

The photocatalytic activity of $Y_2Ti_2O_7$-e photocatalyst calcined at 1100 °C was fourteen times higher than that of $Y_2Ti_2O_7$ photocatalyst prepared using the solid state reaction method. The apparent quantum efficiency was calculated to be ca. 6% at 313 nm, a relatively high value for a water splitting reaction. We also found that the addition of excess Y increased the surface area of $Y_2Ti_2O_7$, as shown in Figure 3. The surface areas of the $Y_2Ti_2O_7$-e samples were larger than those of the $Y_2Ti_2O_7$-s samples at every calcination temperature. We confirmed that the particle size of $Y_2Ti_2O_7$-e was smaller than that of the $Y_2Ti_2O_7$-s by SEM images. The increased surface area is certainly another factor for the higher photocatalytic activities of $Y_2Ti_2O_7$-e compared to $Y_2Ti_2O_7$-s.

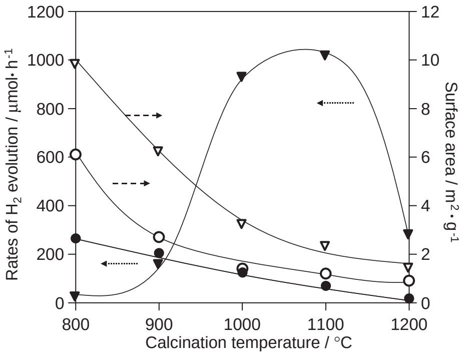

Figure 3. The rates of H_2 evolution (●) and specific surface areas (○) of 1 wt % NiO_x–$Y_2Ti_2O_7$-s samples and the rates of H_2 evolution (▼) and specific surface area (▽) of 1 wt % NiO_x–$Y_2Ti_2O_7$-e samples as a function of calcination temperature.

From these results we conclude that the addition of excess Y effectively prevents the formation of the impurity phase, TiO_2 rutile, which occurs in the stoichiometric preparation of $Y_2Ti_2O_7$ at high calcination temperature and results in a decrease of photocatalytic activity. Consequently, $Y_2Ti_2O_7$ photocatalysts with better crystallinity and higher activity were obtained by the addition of excess Y in the PC method. We could not observe such a significant effect of the Y addition on the photocatalysts prepared by solid state reaction. The modified PC method is useful to develop high activity photocatalyst materials.

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