Stable Photocatalytic Activity of $BaTi_4O_9$ Combined with Ruthenium Oxide for Decomposition of Water

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Barium tetratitanate, $BaTi_4O_9$, combined with ruthenium oxide shows stable photocatalytic activity for the stoichiometric production of hydrogen and oxygen from water.

The development of efficient and stable photocatalysts to decompose water is one of the important topics in light-energy storage. Recently, we showed that the combination of sodium hexatitanate, $Na_2Ti_6O_{13}$, with RuO_2 as a promoter leads to a good photocatalyst for the decomposition of water.[1,2] The interesting feature is that the photocatalyst prepared by oxidation has the ability to produce stoichiometric quantities of hydrogen and oxygen. It is proposed that the characteristic behaviour is associated with the presence of Wadsley–Andersson (W–A) type tunnel structures in $Na_2Ti_6O_{13}$, which consist of the edge- and corner-sharing framework of the TiO_6 octahedron. We have drawn attention to the important role of tunnel structures of transition metal oxides in photocatalysis, and have employed barium tetratitanate, $BaTi_4O_9$, which has the chemical twin type tunnel structures,[3] which differ from the W–A type tunnels. We have found that $BaTi_4O_9$ combined with ruthenium oxide is a new photocatalyst with higher and stable activity for the complete decomposition of water.

Barium tetratitanate was prepared by the calcination of $BaCO_3$ and TiO_2. The formation of the titanate was confirmed by X-ray diffraction. The titanate was impregnated with ruthenium or iridium chloride from respective aqueous solutions. The amount of metal loaded was 3 wt% for ruthenium and 1 wt% for iridium. The impregnated titanates were then subjected to oxidation at 848 K in air for 7 h for activation, which was considered to give rise to the formation of ruthenium oxide and iridium oxide. Hereafter, $BaTi_4O_9$ oxides combined with ruthenium oxide and iridium oxide are referred to as RuO_x/BTO and IrO_x/BTO photocatalysts, respectively. A closed gas-circulation system was used for the photocatalytic reaction. The reaction system was filled with 200 Torr of Ar gas (1 Torr = 133.322 Pa). About 250 mg of photocatalyst was suspended in distilled and deionized pure water of 20 cm^3 by stirring by the Ar gas bubbled through the water. The decomposition reaction was carried out under irradiation of light from an Xe lamp operated at 400 W through a water filter. The evolved gases were analysed by using a gas chromatograph connected to the reaction system.

Fig. 1 shows the photocatalytic reaction with illumination time. Compared to the reaction on the RuO_2-loading $Na_2Ti_6O_{13}$ (referred to as RuO_2/NTO) photocatalyst,[1] the evolution of oxygen began from an initial stage, and the ratio of oxygen to hydrogen almost reached the stoichiometric value ($2O_2/H_2 = 0.96$) in a shorter period. Interestingly, the catalytic activity of RuO_x/BTO photocatalyst at a stationary state was approximately three times higher than that of the RuO_2/NTO photocatalyst. The reaction was repeated three times by evacuating the gas-phase products. Note that the production of H_2 and O_2 was quite reproducible and, the photocatalyst retained the same high activity and ratio of the

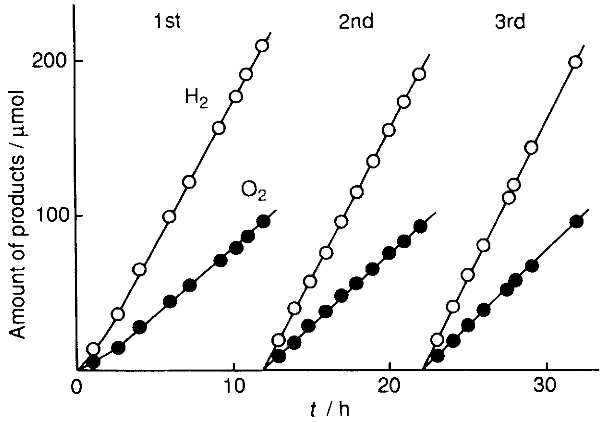

Fig. 1 Stable production of H_2 and O_2 from water by $RuO_x/BaTi_4O_9$ photocatalyst. ○, H_2; ●, O_2.

products, even after 30 h irradiation. There was no trend of deactivation. The number of hydrogen atoms produced during 30 h irradiation was calculated to be approximately 300 times larger than that of the surface Ti atoms.

The stability of the RuO_x/BTO photocatalyst is related to the catalyst preparation in an oxidizing atmosphere, which was different from the activation of the oxide in a reducing atmosphere in conventional TiO_2 photocatalysts. Thus, in the present photocatalytic system, it occurs to a lesser extent that the oxygen produced during water decomposition is incorporated in the lattice of the oxide, which has often been considered as a main cause for the deactivation of the catalyst.

The combination of $BaTi_4O_9$ with iridium oxide also permitted to produce stoichiometrically hydrogen and oxygen, although the activity was lower by a factor of 0.7, compared to that of RuO_x/BTO photocatalyst. The increase in the amount of iridium loaded from 1 wt% to 2 wt% resulted in a drastic decrease in the photocatalytic activity. Instead of $BaTi_4O_9$, a perovskite-type barium titanate, $BaTiO_3$, having no tunnel structures, was taken as another oxide of the Ba–Ti–O phases and was combined with ruthenium oxide, but no photocatalytic activity was observed.

In the structure of $BaTi_4O_9$, the edge- and corner-sharing of TiO_6 octahedron gives rise to the chemical twin tunnels which accommodate the Ba atoms in a pentagonal prismatic coordination. The advantage of the chemical twin tunnel structures in photocatalysis is that they are able to facilitate a strong interaction with ruthenium oxide deposited as a promoter, which is likely to have a favourable effect on the separation of the photoexcited charges and their transfers to the adsorbed reactants.

These results indicate that $BaTi_4O_9$ oxide has potential in developing efficient photocatalysts with stable long-term activity by the combination with the effective promoters. The detailed study on the effects of various promoters and on quantum yield is in progress.

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