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PHOTOCATALYTIC OXYGEN EVOLUTION FROM TiO_2 POWDER - WATER - HALATE SYSTEMS

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Oxygen evolves easily on irradiation($>$300 nm) from aqueous solutions of BrO_3^- and IO_3^- in the presence of TiO_2 around room temperature. By the introduction of this process, the maximum temperature required for several thermochemical cycles for water decomposition is expected to decrease greatly.

The thermal decomposition of IO_3^- or BrO_3^- producing oxygen is included in several thermochemical cycles for water decomposition 1)2) as an oxygen evolution step, which usually requires the highest temperature(500 - 800 °C) of the whole cycle. The replacement of the thermal decomposition by photocatalytic process would help to decrease the maximum temperature required for the cycles greatly. Here, the first example of photocatalytic reaction that can be combined with thermochemical cycles for water decomposition is presented.

It has been found that oxygen evolves easily on irradiation($>$300 nm) from aqueous solutions of BrO_3^- and IO_3^- which are electron acceptors, in the presence of TiO_2(rutile and anatase) around room temperature.

Rutile(Katayama, S.G.) and anatase(Fuji Titan, TP-2) were used as supplied. The reaction was performed in a Pyrex Schlenk tube(108 cm^3) with a rectangular parallelepiped lower part(35 x 35 x 60 mm) and a septum. The reaction mixture consisting of TiO_2 powder(10 mg) and aqueous solution of $KBrO_3$ or KIO_3(0.1 mol/dm^3, 30 cm^3) in an argon atmosphere was irradiated by a 500 W ultra-high-pressure Hg-lamp(Ushio) with stirring. The temperature of the mixture was around 40 °C in the stationary state under irradiation. The concentration of oxygen in the reaction vessel was measured by gaschromatography. The amount of BrO_3^- or IO_3^- remaining in the mixture after the reaction was determined by titration with $Na_2S_2O_3$aq.

Figure 1 shows the amount and the turnover number(mole of O_2/ mole of TiO_2) of the oxygen evolved in the course of the reaction. The turnover number in the case of $KBrO_3$/rutile indicates that the reaction proceeds catalytically for TiO_2. In the cases of $KBrO_3$/rutile, $KBrO_3$/anatase, and KIO_3/rutile, the oxygen evolution almost stopped when the mixture was irradiated through a cut-off filter(Toshiba Glass, L-42, transparent at $\lambda >$420 nm). Since TiO_2 absorbs light shorter than 390 nm and aqueous solution of $KBrO_3$ or KIO_3 does not absorb light longer than 300 nm, it is concluded that the reaction occured through the electrons in the conduction band and the holes in the valence band generated by the photo-excitation of the TiO_2. No oxygen was detected on irradiation in the absence of TiO_2. Both the amount of the oxygen

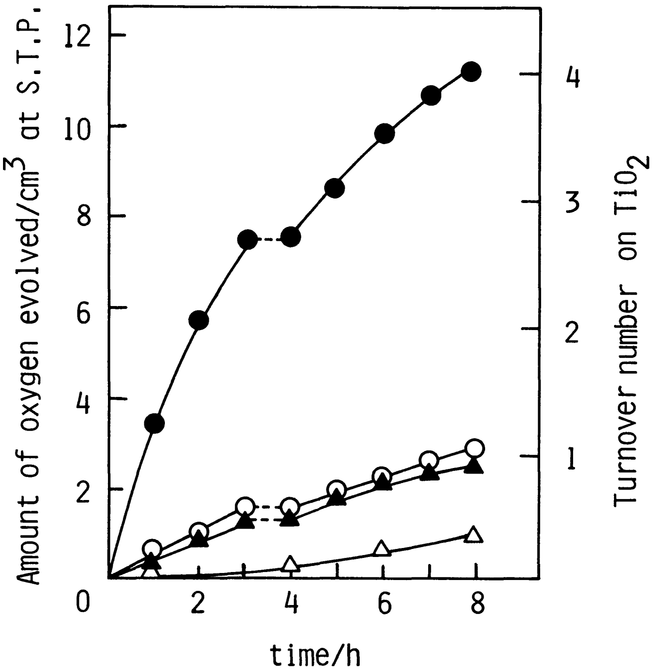

Fig. 1. Amount and turnover number of the oxygen evolved.

● $KBrO_3$/rutile
○ $KBrO_3$/anatase
▲ KIO_3/rutile
△ KIO_3/anatase
--- cut-off filter

evolved and that of the BrO_3^- and the IO_3^- consumed in the presence of the rutile were determined in the experiments other than shown in the Figure. The results are as follows: O_2, 7.35 cm^3 (3.28×10^{-4} mol), BrO_3^- consumed, 2.37×10^{-4} mol; O_2, 12.4 cm^3 (5.54×10^{-4} mol), IO_3^- consumed, 3.17×10^{-4} mol. In both cases the amount of the oxygen evolved are nearly equal to one and a half times those of the halate ions consumed. On the basis of these results, the reaction is assumed to proceed according to the following reaction scheme:

$$TiO_2 \xrightarrow{6h\nu} 6e^- + 6p^+$$

$$6e^- + XO_3^- + 3H_2O \longrightarrow X^- + 6OH^- (X = Br \text{ or } I)$$

$$6p^+ + 6OH^- \longrightarrow 3H_2O + \frac{3}{2}O_2$$

$$\text{overall; } XO_3^- \longrightarrow X^- + \frac{3}{2}O_2.$$

By the use of the present photocatalytic process, for example, the reaction (1) in the Mg-I cycle$^{3)}$ can be replaced by the reaction (2).

$$Mg(IO_3)_2(c) \xrightarrow{700\ °C} MgO(c) + I_2(g) + \frac{5}{2}O_2(g),\ \Delta G° = 0 \text{ at } 313\ °C \quad (1)$$

$$Mg(IO_3)_2\ aq. \xrightarrow[h\nu,\ TiO_2]{r.t.} MgI_2\ aq. + 3O_2,\ \Delta G° = 36.6 \text{ kcal/mol at } 25\ °C \quad (2)$$

The replacement decreases the maximum temperature required for the cycle to around 400 °C.

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