THE SYNERGISM OF β-RAYS AND PHOTONS ON THE PHOTOASSISTED CATALYTIC DECOMPOSITION OF WATER BY Pt/TiO$_2$

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The hydrogen evolution rate in photoassisted decomposition of water by Pt/TiO$_2$ was significantly enhanced in the presence of tritium (90–180 mCi/ml). The extent of the enhancement was proportional to the tritium concentration. This effect is attributed to the synergism of β-rays from tritium and photons on this decomposition reaction.

1. Introduction

The application of solar energy has recently been extensively studied. Among a variety of applications, great interest has been aroused in the photoassisted catalytic decomposition of water, the water–gas shift reaction, and so on [1–4]. These reactions can also be applied to the concentration and/or recovery of tritium from tritiated water, which is one of the important problems concerning heavy-water moderated fission reactors [5] and in controlled thermonuclear fusion reactors. From these viewpoints, we studied the kinetics of the photoassisted decomposition of water by platinized TiO$_2$ (anatase). We found that the presence of tritium in water significantly enhanced the photoassisted decomposition of water. The extent of the enhancement was proportional to the tritium concentration in water. This phenomenon arises from neither radiolysis by β-rays nor the well-known radiation-induced catalysis observed by many investigators [2,6–10]. It is a newly observed phenomenon caused by the synergism of β-rays and photons.

2. Catalyst preparation and procedures

Titanium dioxide (anatase) was prepared by following Kurosaki et al. [11]. An aqueous solution of TiCl$_4$ (0.33 M) was hydrolyzed with 3 N ammonia solution at 273 K. The titanium oxide–hydroxide gel obtained was filtered and washed, dried at 397 K for one day, and calcined at 873 K for 4 h in air. Platinized TiO$_2$ ($\approx$ 0.6 wt%) was prepared by following Courbon et al. [12]. An aqueous solution of H$_2$PtCl$_6$ (1.7×10^{-2} M) was added to the TiO$_2$ powder drop by drop with magnetic stirring. Subsequently, the powder was dried at 373 K and oxidized with air at 873 K for 2 h. It was degassed for 30 min in vacuo, reduced for 2 h with H$_2$ at 40 KPa, and degassed for 30 min in vacuo: the temperature was kept at 823 K during this process. The anatase structure was confirmed with X-ray diffraction. The BET surface area was determined as 30 m^2/g by nitrogen adsorption at 77 K. The average particle size of catalyst was evaluated as $\approx$ 300 Å from X-ray diffraction, BET surface area, and scanning electron microscopic observation.

Reactant water was ordinary distilled water (H$_2$O) or tritiated water (H$_2$O/HTO). The latter was prepared by diluting the tritiated water (H$_2$O/HTO, 1 Ci/ml) purchased from New England Nuclear Co. with distilled ordinary water.

The apparatus for measuring the reaction rate of hydrogen evolution consisted of a reaction vessel made of a quartz glass, a gas sampling system to which a McLeod gauge and gas sampling tube were attached, and a vacuum system. Those components were connected to each other with copper tubing. A deuterium lamp (Hamamatsu Photonics, L-544: 190–300 nm, 30 W) was used as photon source.

The platinized TiO_2 powder of 0.3 g was added to 5 ml of the reactant water (H_2O or H_2O/HTO) in the reaction vessel. The reactant water was carefully degasses by repeating a freeze–evacuation cycle three times. The catalyst was magnetically dispersed in the reactant water and illuminated with the deuterium lamp which was about 2 cm distant from the reaction vessel. The temperature was kept constant at 298 ± 3 K by a water bath. The total pressure of the product gas was measured by the McLeod gauge via a cold trap at 77 K to condense water vapor in the sampling gas. In addition, the gas was analyzed by a radio-gas-chromatograph with use of the sampling tube. For this purpose, a $FeCl_3$/activated Al_2O_3 column (3 mm diameter) with 1.0 m length was used at 77 K. The radio-gas-chromatograph had been calibrated against hydrogen isotopes (H_2, D_2, HD, and HT).

3. Decomposition of ordinary water

The illumination of the catalyst in water caused hydrogen (H_2) evolution. However, no oxygen evolution was detected in the present experimental conditions. This was also true for tritiated water. This is because oxygen is adsorbed on TiO_2 surface till saturation of adsorption sites [13], or H_2O_2 is formed in reactant water [2,3]. The hydrogen evolution for ordinary water is shown by curve (a) in fig. 1. The evolution rate decreased gradually to reach to a steady value. The initial reaction rate, which is defined as the amount of evolved hydrogen (H_2) in the first hour in the present study, was 0.55 μmol/h. The observed initial reaction rate was within the range of those observed by other investigators (for example, ref. [14]). Without the illumination, no hydrogen was evolved. In addition, illumination of the reactant water in the absence of the catalyst also produced no hydrogen. The results indicate that the Pt/TiO_2 prepared in the present study has the similar catalytic properties as those of the catalysts used by other investigators [1–4].

4. Decomposition of tritiated water

Case 1: When the illumination of the catalyst was performed in the tritiated water whose tritium concentration, [HTO], was 6.2×10^{-3} M (equivalent to 180 mCi/ml), H_2 and HT were evolved. The hydrogen (H_2) evolution is shown by curve (b) in fig. 1. The observed initial reaction rate was 4.92 μmol/h. This is approximately nine times higher than that observed for ordinary water (H_2O), indicating that the reaction was enhanced in the presence of tritium.

Case 2: Curve (c) in fig. 1 shows hydrogen (H_2) evolution from the tritiated water whose tritium concentration was 90 mCi/ml. The initial reaction rate, which is the hydrogen (H_2) evolution in the first hour as mentioned above, was determined as 2.72 μmol/h. This value was five times higer than that for ordinary water.

Case 3: Without illumination of the catalyst in the tritiated water of 90 mCi/ml, hydrogen evolution was also observed: the hydrogen (H_2) evolution was shown by the dotted line in fig. 1. The initial reaction rate was determined as 0.02 μmol/h. This is about 1/30

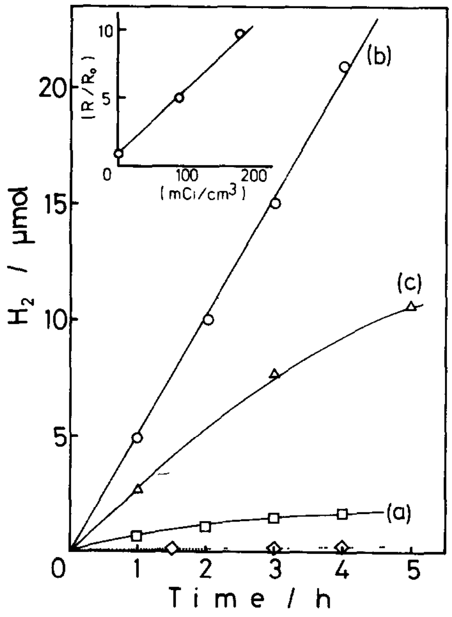

Fig. 1. Time course of the hydrogen (H_2) evolution over Pt/TiO_2 at 298 K; reactant (a) H_2O, (b) H_2O/HTO (180 mCi/ml), and (c) H_2O/HTO (90 mCi/ml). The dotted line is for hydrogen evolution in cases 3, 4, and 5. The inset shows a relationship between the extent of the enhancement of reaction rate and radioactivity of tritiated water (H_2O/HTO): for R and R_0, see text.

of the photoassisted decomposition of the ordinary water.

Case 4: The photon illumination of the tritiated water of 90 mCi/ml in the absence of catalyst gave rise to hydrogen evolution at the rate in the same order of magnitude as that observed in case 3.

Case 5: A comparable amount of hydrogen evolution was also observed for the tritiated water of 90 mCi/ml in the absence of catalyst and illumination.

There was no appreciable difference in the initial reaction rates among cases 3, 4 and 5. They are shown by the dotted line in fig. 1. The results indicate that the radiolysis of water took place in the tritiated water due to β-rays from tritium decay. However, the rate of radiolysis was far smaller than that of the photassisted decomposition of ordinary water.

The above observations indicate that the enhancement of the reaction rate observed in cases 1 and 2 differs from the well-known radiation-induced catalytic reactions observed by many investigators [2,6–10]: that is, the catalytic activity is enhanced by only the irradiation of γ-rays or neutrons in these cases. The enhancement of the reaction rates observed in cases 1 and 2 apparently arises from the synergism of β-rays and photons on the catalytic reaction.

The extent of the synergism seemed to be proportional to the radioactivity of the reactant water. The relation between the tritium concentration and the extent of the enhancement of reaction rate, R/R_0, is shown in the figure inset, where R and R_0 are the initial reaction rates in the tritiated water (H_2O/HTO) and non-radioactive ordinary water (H_2O), respectively.

Although it is premature to discuss in detail the mechanism of the synergistic effect, it is considered as follows. The photassisted decomposition of water is a result of the excitation of the valence band electrons of TiO_2 by the photon illumination [1–4]. The electrons excited to the conduction band move to the Pt-surface where the reduction of hydrogen ions takes place. The holes in the valence band react with water molecules or hydroxyl groups to produce oxygen and/or hydrogen peroxide. The observation in cases 3–5 indicates that the β-rays from tritium do not cause the ionization of the valence band electrons. However, the β-rays may produce secondary electrons. These electrons and β-rays themselves lose their energy by scattering and are eventually trapped by lattice defects or impurities. It is also plausible that solvated electrons are adsorbed on the catalyst to leave trapped electrons on the surface. These electrons may be excited to the conduction band by the photon illumination to enhance water decomposition.

Further investigations will have to be carried out to understand this β-ray induced photoassisted decomposition of water. On account of the above consideration, however, the similar synergism of photons and β-rays (or energetic electrons from artificial electron sources) is expected to take place not only for photoassisted catalytic reactions, but also for other photoconductive processes such as photoelectricity, light amplification, and so on.

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