Light-intensity dependence in photocatalytic decomposition of water over $K_4Nb_6O_{17}$ catalyst

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Received 14 May 1994; accepted 18 June 1994

We have measured, for the first time, the light-intensity dependence in photocatalytic decomposition of water over $K_4Nb_6O_{17}$. In higher light-intensity region, the rate of reaction is proportional to the square root of the light intensity. In lower light-intensity region, on the contrary, the rate is almost linearly proportional to the light intensity. We propose a reaction model whose main path of the reaction loss is the recombination of the charges generated under band-gap radiation. This model describes the light-intensity dependence of this reaction well.

Keywords: photocatalysis; water decomposition; light-intensity dependence; $K_4Nb_6O_{17}$

1. Introduction

Recently, some researchers have reported overall water splitting into H_2 and O_2 on several oxide-photocatalysis systems [1–9]. $K_4Nb_6O_{17}$ shows a quantum efficiency of ca. 0.053 [6], which is noticeably high for this reaction. However, there are only a few quantitative analyses of the reaction mechanism, not only for $K_4Nb_6O_{17}$ but also for others [10–13]. The rate of the charge generation changes according to the light intensity; thus it is meaningful to evaluate the reaction activity under various light intensities.

This paper will report the evaluation of the light-intensity dependence of water-splitting reactions over $K_4Nb_6O_{17}$ without metal or metal oxide loading based on comparative experiments in two different light-intensity regions. We will discuss a

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reaction model whose main path of the reaction loss is the recombination of the positive and negative charges generated by the absorption of band-gap light.

2. Experimental

$K_4Nb_6O_{17}$ powder catalyst was prepared as follows. A mixture of K_2CO_3 (4.53 g) and Nb_2O_5 (10.00 g) was melted in a platinum crucible (50 mm diameter) at 1523 K in air. An excess potassium acts as flux. The melt was kept at 1523 K for 24 h, and controlled to cool down at a rate of 10 K h^{-1} to 1173 K, then left to cool down. The mixture formed into two phases of solid. Crystal grains of $K_4Nb_6O_{17}$ were at the upper phase of the solid. These crystals were crushed into powder and used as the $K_4Nb_6O_{17}$ photocatalysts. The crystal structure was confirmed by X-ray diffraction [14].

The catalysis activity was measured in a glass closed gas circulation system. We used greaseless stopcocks which consisted of glass cylinders, Teflon pistons and Viton O-rings. O_2 leakage from outside of the system was about 15 nmol/h. We employed a quartz photoreactor (200 ml) with water cooling jacket to obtain constant temperature at any light-intensity. The catalyst (1.00 g) was suspended in the distilled water (200 ml) by a magnetic stirrer. After the gas circulation system and the reactant were sufficiently degassed, we introduced Ar gas (4×10^4 Pa) to the system as the carrier and started the reaction.

We used a high-pressure Hg lamp system (USHIO, SPOT CURE, 250 W) for measurements at the higher light-intensity region. The light of the Hg lamp was collected by a miller in order to minimize the loss. For the measurement at the lower light-intensity region, we used a constant energy monochromatized lighting system (NIKON, CES-3S, Xe 150 W). In both regions, the light was irradiated from a side to the reaction cell. In the higher light-intensity region, we inserted neutral-density filters (ND-filter) between the reaction cell and the lighting system to control the light intensity, and the light intensity was estimated as the sum of the intensities of the light whose photons have energies bigger than the band-gap energy of $K_4Nb_6O_{17}$ (3.5 eV). The irradiated area at higher light-intensity region was about 7 cm^2. In the lower light-intensity region, we changed the light intensity in the range of 2.0 to 25.0 $\mu W/cm^2$; the wavelength of the light was 300 nm and the irradiated area was 2.25 cm^2.

We analyzed the evolved gases by gas chromatography (Ar carrier, TCD) with a molecular sieve 5A column, which was attached directly to the gas circulation system.

3. Results and discussion

Fig. 1 shows the light-intensity dependence of the water decomposition reaction at the higher light-intensity region. The evolution rate of H_2 (v_{H_2}) was propor-

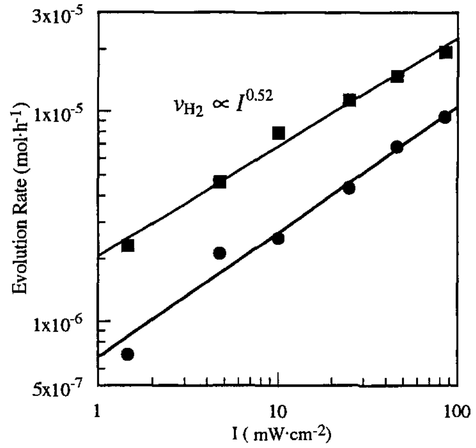

Fig. 1. The light-intensity dependence of the water decomposition reaction at higher light-intensity region: (■) H_2, (●) O_2. Light source: high-pressure Hg lamp (250 W). Catalyst = $K_4Nb_6O_{17}$ (1.0 g). Reactant = distilled water (200 ml).

tional to the square root of the light intensity (I), $v_{H_2} \propto I^{0.52}$. In the reaction, we observed even O_2 along with H_2; however, the observed H_2/O_2 ratio was 2.1–3.3, which was little larger than the stoichiometric one. This tendency was emphasized as light intensity became lower.

Fig. 2 shows the light-intensity dependence of the water decomposition reaction at the lower light-intensity region. The evolution rate of H_2 was almost linearly proportional to the light intensity, $v_{H_2} \propto I^{0.92}$, contrasting with the higher light-intensity region. Although this experiment was performed with the distilled water alone, no significant O_2 was observed except the leakage from outside of the system

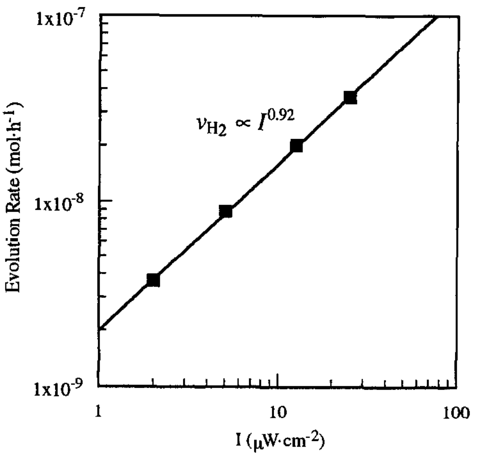

Fig. 2. The light-intensity dependence of the water decomposition reaction at lower light-intensity region. Light source: a constant-energy monochromatized lighting system (Xe lamp, 150 W); wavelength = 300 nm; irradiated area = 2.25 cm^2.

(15 nmol/h). Before the experiment, it had been confirmed that the mixture of catalyst and distilled water had been able to produce H_2 and O_2 simultaneously at the higher light-intensity region, so the lack of O_2 cannot be based on organic impurities. The lack of O_2 may be attributed to the photoadsorption of the oxygen on the catalyst.

To describe the two types of light-intensity dependence, we propose a model that has two parallel reaction pathways. One path is a reaction of water with electron (e^-) and positive hole (h^+), both generated by the absorption of band-gap light:

$$h\nu \rightarrow e^- + h^+ \tag{1}$$

$$e^- + H^+ \rightarrow \tfrac{1}{2}H_2 \tag{2}$$

$$h^+ + \tfrac{1}{2}H_2O \rightarrow H^+ + \tfrac{1}{4}O_2\,, \tag{3}$$

where $h\nu$ is the energy of an absorbed photon. The other is the recombination of electrons and holes:

$$e^- + h^+ \rightarrow E_{\mathrm{recom}}\,, \tag{4}$$

where E_{recom} is the relaxation energy of recombination. The total concentration of negative charge can be written as $n = n_{\mathrm{photo}} + n_{\mathrm{dark}}$, where n_{dark} is the concentration under dark condition (i.e., thermal equilibrium condition), and n_{photo} is the increment of the charge concentration caused by the light absorption. In the same way, the total concentration of positive charge is expressed by $p = p_{\mathrm{photo}} + p_{\mathrm{dark}}$, where p_{dark} is the concentration of positive charge under dark condition, and p_{photo} is the increment of the charge concentration by the light absorption.

At steady state, the reaction rate described in eq. (2) (v_{react}) is the same as the reaction rate described in eq. (3); therefore, the following equation can be introduced:

$$v_{\mathrm{react}} = k_{n,\mathrm{react}} n_{\mathrm{photo}} = k_{p,\mathrm{react}} p_{\mathrm{photo}}\,, \tag{5}$$

where $k_{n,\mathrm{react}}$ is the rate constant of the reaction in eq. (2), $k_{p,\mathrm{react}}$ is the rate constant of the reaction in eq. (3). When we assume the rate of photon absorption to be the rate of charge generation, the rate of photon absorption (v_{ab}) can be the same as the sum of the rate of the reaction and the rate of the recombination (v_{recom}). Therefore,

$$v_{\mathrm{ab}} = v_{\mathrm{react}} + v_{\mathrm{recom}}\,. \tag{6}$$

v_{recom} can be expressed by

$$\begin{aligned} v_{\mathrm{recom}} &= k_{\mathrm{recom}}(np - n_{\mathrm{dark}} p_{\mathrm{dark}}) \\ &= k_{\mathrm{recom}}(n_{\mathrm{photo}} p_{\mathrm{photo}} + n_{\mathrm{dark}} p_{\mathrm{photo}} + n_{\mathrm{photo}} p_{\mathrm{dark}})\,. \end{aligned} \tag{7}$$

From eqs. (5)–(7), we get the relation between v_{ab} and v_{react}:

$$v_{\mathrm{ab}} = \frac{k_{\mathrm{recom}}}{k_{n,\mathrm{react}}k_{p,\mathrm{react}}} v_{\mathrm{react}}^2 + \left(1 + \frac{k_{\mathrm{recom}}}{k_{p,\mathrm{react}}}(n_{\mathrm{dark}} + p_{\mathrm{dark}})\right) v_{\mathrm{react}} \,. \tag{8}$$

When the light intensity is high enough to ignore the second term of the right-hand side of eq. (8), the reaction rate can be described as

$$v_{\mathrm{react}} \approx \sqrt{\frac{k_{n,\mathrm{react}}k_{p,\mathrm{react}}}{k_{\mathrm{recom}}} v_{\mathrm{ab}}} \,, \tag{9}$$

which shows that the rate of reaction should be proportional to the square root of the light intensity in the higher light-intensity region. This conclusion is in good agreement with the experimental results shown in fig. 1.

On the other hand, when the light intensity is low enough to ignore the first term of the right side of eq. (8), v_{react} is obtained as

$$v_{\mathrm{react}} \approx \left(1 + \frac{k_{\mathrm{recom}}}{k_{p,\mathrm{react}}}(n_{\mathrm{dark}} + p_{\mathrm{dark}})\right)^{-1} v_{\mathrm{ab}} \,. \tag{10}$$

Therefore, the rate of reaction should be proportional to the light intensity in the lower light-intensity region, as confirmed experimentally in fig. 2.

From the results of the lower light-intensity region (fig. 2), the maximum value of the quantum efficiency can be estimated to be 0.20 using the following equations:

$$\phi = \frac{v_{\mathrm{H_2}}\ (\mathrm{mol/h})/3600 \times 6.02 \times 10^{23}}{v_{\mathrm{ab}}\ (/\mathrm{s})} \times 2 \tag{11}$$

and

$$v_{\mathrm{ab}}\ (/\mathrm{s}) = I\ (\mathrm{W/cm^2}) \times \text{irradiated area } (\mathrm{cm^2}) \times \frac{1}{h\nu(J)} \times 0.92 \text{ (transmittance of glass window)} \,. \tag{12}$$

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