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Photocatalytic properties of gallium oxides prepared by precipitation methods toward the overall splitting of H_2O

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ABSTRACT

The photocatalytic properties of gallium oxides that were prepared by precipitation methods to the overall splitting of H_2O were studied. The photocatalytic behavior of the NiO-loaded gallium oxides to this reaction could be separated into three categories on the basis of the preparation temperatures of the gallium oxides. The photocatalytic behavior of each category reflected the behavior of corresponding crystal phase of gallium oxides. Of these categories, NiO-loaded α-Ga_2O_3, which composed the second category, exhibited remarkably high photocatalytic activity compared with those of NiO-loaded GaO(OH) and NiO-loaded β-Ga_2O_3 which composed the first and third categories, respectively. Through investigations, such as the characterization of the prepared gallium oxides, the effects of combining $Rh_yCr_{2-y}O_3$ co-catalyst with the photocatalytic activity and the effects of the preparation methods on the photocatalytic reaction, the influences of the states and the morphologies of the gallium oxide photocatalysts to the photocatalytic overall splitting of H_2O were discussed.

1. Introduction

Photocatalytic overall splitting of H_2O over semiconductive catalysts is one of the fundamental photocatalytic reactions since electrons and holes produced by photo-irradiation directly contribute to the reduction and oxidation of H_2O. Moreover, this reaction has high positive Gibbs free energy under standard pressure at ambient temperature. This means that photoenergy directly converts into chemical energy if the reaction proceeds by using photocatalysts. Therefore, photocatalytic water splitting is one of the important photocatalytic reactions and has been widely studied to find an effective photocatalyst for the reaction [1,2]. Up till now, various oxides, consisting of transition metal ions with d^0 electron configurations such as the oxides of Ti, Zr, Nb, and Ta, and oxides with d^{10} electron configurations such as the oxides of Ga, Ge, In, Sn, and Sb have been reported as showing photocatalytic activity to this reaction [2]. However, photocatalytic performances, such as photoresponse as well as photocatalytic activity, are insufficient for practical applications. Next, investigations to improve the photocatalytic performances to the overall splitting of H_2O, particularly, the improvement of photocatalytic activity and photoresponse, have been carried out [3–13]. In particular, remarkably high photocatalytic activity of the overall splitting of H_2O was reported to be achieved on NiO-loaded $NaTaO_3$ by doping La ion [3,4]. The effects of La ion doping on $NaTaO_3$ for improving the photocatalytic activity were also reported [4].

On the other hand, Ga_2O_3, one of the oxides consist of the metal ions of p-block elements with d^{10} electron configuration, has been reported to exhibit photocatalytic activity to the overall splitting of H_2O and related photocatalytic reactions [14,15]. The photocatalytic activities, however, were not so high though the electrons and the holes produced under irradiation had sufficient potential for the production of H_2 and O_2 from the reduction and oxidation of H_2O. Then, various modifications to Ga_2O_3 were examined in order to improve the photocatalytic performance [16–19]. Particularly, we have demonstrated remarkable improvement in the photocatalytic activity of β-Ga_2O_3 to the overall splitting of H_2O by modifying the bulk and surface of β-Ga_2O_3, such as the addition of metal ions, and by changing the morphology by controlling the preparation conditions and the combination of the effective co-catalyst [17,18]. Consequently, $Rh_yCr_{2-y}O_3$-loaded Zn-ion-doped β-Ga_2O_3, where β-Ga_2O_3 was prepared by the ammonia precipitation method, exhibited remarkably high photocatalytic activity on the overall splitting of H_2O [17,18], and the level of the photocatalytic activity was the same as that of NiO-loaded La-doped $NaTiO_3$ [4]. Recently, the improvement of the photocatalytic activity of Ga_2O_3 of the overall splitting of H_2O was observed on a Ga_2O_3 photocatalyst prepared by the ammonia precipitation method [20]. Here, the improvement of the photocatalytic activity

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was confirmed by improving the charge separation that originated with the formation of a junction between α-Ga_2O_3 and β-Ga_2O_3 over the photocatalyst surface.

From previous studies, precipitation methods, in particular, the ammonia precipitation method, are important methods for preparing the Ga_2O_3 photocatalyst for the overall splitting of H_2O. However, the photocatalytic properties of Ga_2O_3 prepared by precipitation methods have not been investigated so far.

In this study, we investigate the photocatalytic properties of gallium oxides prepared by precipitation methods toward the overall splitting of H_2O. Here, the photocatalytic abilities of gallium oxides with various crystal phases were reported on the basis of the examination of the preparation conditions and effects of the combined co-catalysts.

2. Experimental

2.1. Preparation of Ga_2O_3 photocatalysts

Ga_2O_3 used in this study was prepared by two kinds of precipitation methods. One is the method which uses aqueous ammonia as the precipitant (ammonia precipitation method), and the method which uses urea as the precipitants (urea precipitation method). With the ammonia precipitation method, hydrolysis of $Ga(NO_3)_3$ (High Purity Chemical) was carried out by dropping aqueous ammonia onto $Ga(NO_3)_3$ aqueous solution at 298 K until the pH value of the supernatant solution became 9 to obtain the precipitate of gallium hydroxide. On the other hand, hydrolysis was carried out in the aqueous solution of $Ga(NO_3)_3$ and urea where a relatively large amount of urea (10 times in molar ratio) dissolved in $Ga(NO_3)_3$ aqueous solution at 343 K. The obtained gallium hydroxide was calcined at prescribed temperatures to prepare gallium oxide. The prepared gallium oxides were used as the photocatalyst after combining with a NiO or $Rh_yCr_{2-y}O_3$ co-catalyst. NiO-supported gallium oxides were prepared by the impregnation method by using $Ni(NO_3)_2$ aqueous solution. The $Ni(NO_3)_2$-supported gallium oxide was prepared below 353 K by using a rotary evaporator and calcined in air at 473 K for 3 h to prepare NiO-supported gallium oxide. $Rh_yCr_{2-y}O_3$-supported gallium oxides were also prepared by the impregnation method according to earlier reports.

2.2. Photocatalytic reaction

Photocatalytic reactions were performed in an inner-irradiation type photoreaction cell made of quartz. The cell was connected to a closed gas circulation system. The system was equipped with a vacuum line and a sample inlet for gas chromatography. The photocatalyst (1 g) was suspended in well-degassed deionized H_2O (650 ml) in the cell, and irradiation was carried out by using a high-pressure Hg lamp (450 W USHIO). The evolved gases were collected in a sampling tube and analyzed by a gas chromatograph (Shimadzu GC-8A).

2.3. Evaluation of quantum yield

The apparent quantum yield (AQY) for photocatalytic H_2O splitting was measured by using a top-irradiation type photoreaction cell connected to a closed gas circulation system. Irradiation was carried out by a 450 W high-pressure Hg lamp through a water-cooling jacket made of quartz, a slit with 20 mm in diameter, and a band pass filter ($\lambda = 254$ nm, obtained from Edmond optics). The incident photocurrent was measured by using a calibrated silicon photodiode (HAMAMATSU Photonics) at the level of the water–gas interface, and the photon flow was calculated by the photocurrent. The AQY was estimated from the following equation:

$$\mathrm{AQY}\ (\%) = (\text{Number of photons used for the overall splitting of } H_2O) \times 100/(\text{Number of incident photons})$$

2.4. Characterization

The surface area of the photocatalysts was evaluated from the isotherm of N_2 adsorption by the BET method. The photocatalysts were characterized by UV–Vis diffuse reflectance spectroscopy (Jasco. U-best 550DS), XRD (Rigaku Rint-2200), and FE-SEM (Hitachi S-4800).

3. Results and discussion

3.1. Photocatalytic properties of gallium oxides prepared by the ammonia precipitation method

Fig. 1 shows the evolution of H_2 and O_2 from H_2O in time over NiO (4 wt%)-loaded gallium oxide photocatalysts, which were prepared by calcining gallium hydroxide precipitate, obtained by the ammonia precipitation method, at (a) 523 K, (b) 598 K, and (c) 773 K for 10 h. From the results in Fig. 1, the production of H_2 and O_2 in stoichiometric ratio can be confirmed on all photocatalysts. Photocatalytic activity is defined as the amount of evolved H_2 and O_2 per hour under a steady state. It is also observed in Fig. 1 that the photocatalytic activity markedly improves while the preparation temperatures are increased. Then, the relation between the photocatalytic activity of NiO (4 wt%)-loaded gallium oxide to splitting of H_2O and the preparation temperatures was examined. The results are shown in Fig. 2.

Fig. 2 shows the photocatalytic activity of NiO (4 wt%)-loaded gallium oxide as a function of the preparation temperatures of the gallium oxides. As shown in Fig. 2, it is observed that the photocatalytic activity of gallium oxide to water splitting strongly correlated with the preparation temperature. The gallium oxide photocatalysts, prepared under 523 K show low activity, while photocatalytic activity improves markedly if gallium oxide prepared at 598 K is applied. The photocatalysts prepared between 598 K and 823 K show markedly high photocatalytic activity, while photocatalytic activity remarkably decreases if the photocatalysts prepared over 873 K are applied. From the results in Fig. 2, the photocatalytic properties of the prepared gallium oxide can be categorized into three groups on the basis of the preparation temperatures. The first category is the gallium oxide prepared

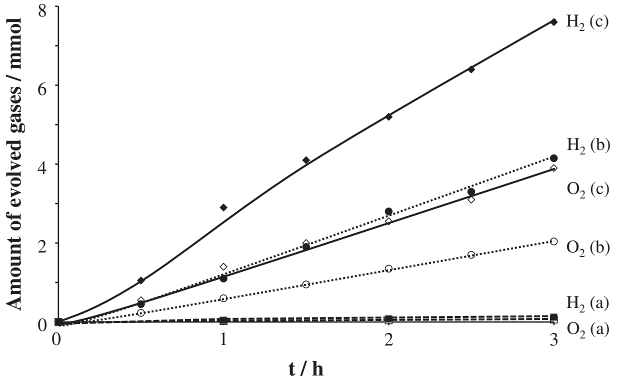

Fig. 1. Evolution of H_2 and O_2 in time over various NiO (4 wt%)/gallium oxide photocatalysts, where gallium oxides are prepared by the ammonia precipitation method and obtained by calcination at (a) 523 K, (b)598 K, and (c) 773 K.