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LETTERS

Silver Bromide as a Photocatalyst for Hydrogen Generation from CH_3OH/H_2O Solution

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A $AgBr/SiO_2$ catalyst prepared from Schumann emulsion has been used for photolysis of CH_3OH/H_2O solution. Under UV illumination, H_2 generation was observed and hydrogen was continuously evolved for 200 h without destruction of AgBr although Ag^0 was detected by X-ray diffraction analysis after the reaction. It is presumed that the hydrogen production from methanol in distilled water occurs on the Ag^0 and the support plays important roles for the photocatalysis as well as TiO_2/SiO_2 (*J. Phys. Chem. B* **1997**, *101*, 2611).

Introduction

Silver halides are well-known as photosensitive materials and widely employed as source materials in photographic films. The photographic process in silver halides comprises basically the following: Absorption of a photon liberates an electron and a positive hole. The electron will combine with a mobile interstitial silver ion, leading to separation of a silver atom. Upon repeated absorption of photons, ultimately a cluster of silver atoms can be formed. This is the so-called latent-image speck. The critical size, which was investigated by Fayet et al.,[1] is four silver atoms for the development. This means that silver halides are unstable under irradiation of light, leading to the color change of silver halide after the exposure to sunlight. From those properties, silver halides have not been so much subjected to studies on the photolysis of water such as TiO_2[2] and CdS.[3]

Recently, Calzaferri et al.[4] reported that thin silver chloride layers on SnO_2-coated glass plates evolved O_2 in the presence of small excess Ag^+ ions in aqueous solution under near-UV illumination. The role of Ag^+ ions was to supply AgCl species to perform continuous photooxidation of water. This indicates that silver halides have a potential for water splitting under irradiation if we can discover a suitable condition to avoid the photodecomposition of silver halides. We have thus employed supported-silver halide catalysts to investigate whether or not the photosensitivity can be available for water decomposition.

In this study, AgBr, which was prepared using a Schumann emulsion[5] described in the film technology, was dispersed on silica support and CH_3OH/H_2O solution was employed to examine the photocatalytic activity. The formation of H_2 was observed, and H_2 was continuously evolved even after UV illumination for 200 h.

Experimental Section

AgBr emulsion was prepared according to the preparation method for a Schumann dry plate,[5] which is widely used for an UV-sensitive photograph, because UV light was employed in all experiments. In brief, two solutions were prepared: Adequate amounts of potassium bromide and gelatin were dissolved in distilled water at 373 K (solution A) and an adequate amount of $AgNO_3$ was also dissolved in distilled water at 373 K (solution B). Solution B was slowly poured into solution A under vigorous stirring, and the mixed solution was kept at 373 K for 30 min under mild stirring. Next, the mixed solution was cooled with ice for 2 h to form gel, and then the gel pieces were wrapped with a cloth to wash with flowing water for 2 h. After washing, the solid pieces were completely dissolved in distilled water at 368 K. Finally, AgBr emulsion was prepared by filtration using a funnel packed with glass wool.

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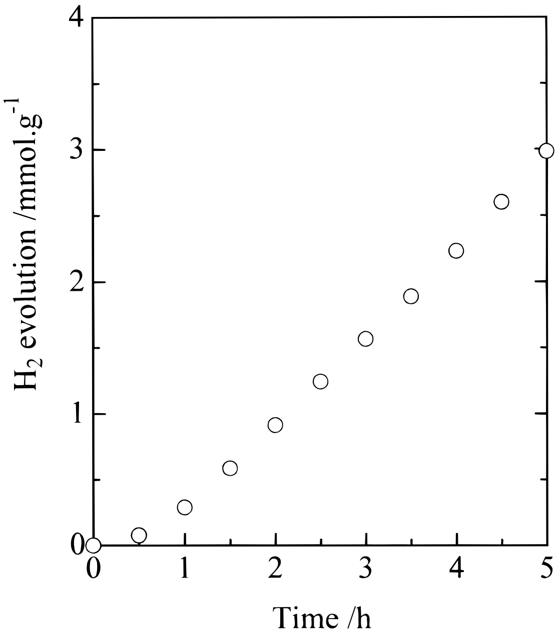

Figure 1. Hydrogen evolution on $AgBr/SiO_2$ catalyst from CH_3OH/H_2O.

$AgBr/SiO_2$ catalyst was also prepared as follows: An adequate amount of AgBr emulsion and distilled water were added to SiO_2 (Aerosil 300, Nippon Aerosil Co.), and then the mixture was stirred until AgBr was dispersed homogeneously. $AgBr/SiO_2$ powder obtained by vacuum evaporation was dried at 383 K for 24 h. Finally, the powder was calcined at 773 K for 3 h. BET surface area and Ag content were 125 $m^2\ g^{-1}$ and 10 wt %, respectively. The catalyst prepared was wrapped with an aluminum film to avoid exposure to light because AgBr was a photosensitive material.

The photocatalytic activity was examined using an inner-irradiation type quartz cell with a 100 W high-pressure Hg lamp-(USHIO Inc.). An amount of 0.2 g of $AgBr/SiO_2$ catalyst was suspended with 300 mL of methanol/distilled water(volume ratio, 1:1), followed by thorough deaeration by bubbling with Ar for 1 h. The suspension, where the solution temperature was kept at room temperature using a water bath, was stirred continuously under Ar flow with 20 mL min^{-1} and irradiated through a water filter for removing IR radiation. Hydrogen was analyzed by gas chromatography (Shimazu GC-8) using a column packed with Molecular Sieves 5A. Ag/SiO_2 catalyst was also characterized by X-ray diffraction (Rigaku, RINT 1000) and UV−vis diffuse reflectance spectroscopy (Shimazu, UV-2400PC).

Results and Discussion

An XRD spectrum of the $AgBr/SiO_2$ catalyst showed sharp diffraction peaks assigned to AgBr[6] and a broad peak corresponding to amorphous SiO_2. The UV−vis spectrum also implied that there was a strong increase in absorbance at 450 nm corresponding to the indirect band gap as well as a strong absorption peak around 290 nm assigned to the direct band gap of AgBr.[7] Those indicate that the dispersed AgBr crystallites on SiO_2 possess almost the same photoproperty reported in the literature.[8]

The catalyst was subjected to the photolysis of the CH_3OH/H_2O solution. The result is shown in Figure 1. H_2 was continuously evolved with the illumination time. On the other hand, we presume that CO_2 might be formed as the oxidation product according to a previous report using $RuO_2/TiO_2/Pt$ catalyst.[9] The formation rate of H_2 was estimated to be 0.65 mmol $h^{-1}\ g^{-1}$. The total amount of H_2 per 1 mol of AgBr was beyond 1.0 even after 2 h, indicating that the reaction seems to occur catalytically and the photodegradation of AgBr seems to be inhibited. It is noted that the activity of H_2 production was poor when distilled water only was used as a trial. This suggests that CH_3OH acts effectively for hydrogen formation. The effect of UV illumination was also investigated. As shown in Figure 2, H_2 evolution stopped in the absence of UV illumination. However, after the UV light was used for irradiation again, H_2 evolution recommenced with the same formation rate, showing that the reaction is induced by the absorption of UV light. The durability of $AgBr/SiO_2$ catalyst is given in Figure 3. The H_2 production continued even after 200 h, although the formation rate somewhat decreased. Total volume of evolved H_2 was attained to 445 mmol per g of AgBr, whose value was corresponded to 84 mol per mol of AgBr. This result contains important evidence because it is generally accepted in the photographic field that silver halides are easily decomposed by light absorption to form silver metals as the latent image center.

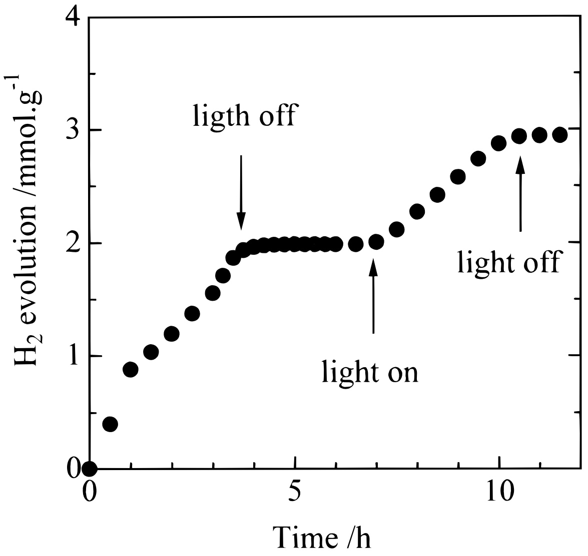

Figure 2. Effect of UV illumination for hydrogen evolution on $AgBr/SiO_2$ catalyst from CH_3OH/H_2O.

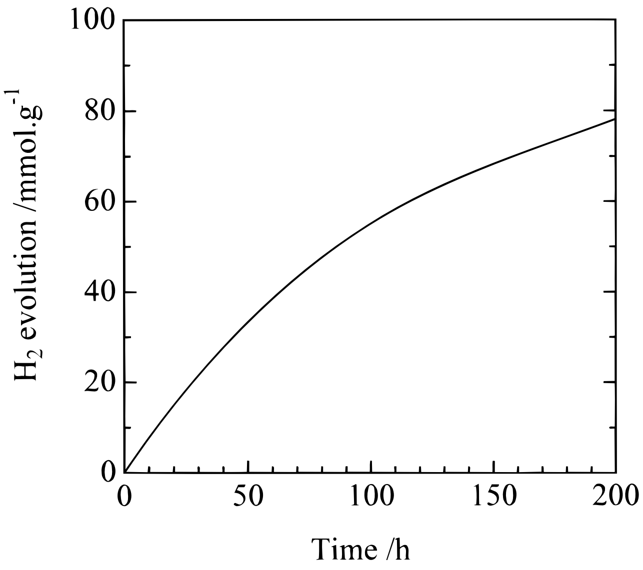

Figure 3. Behavior of hydrogen evolution on $AgBr/SiO_2$ catalyst from CH_3OH/H_2O for 200 h.

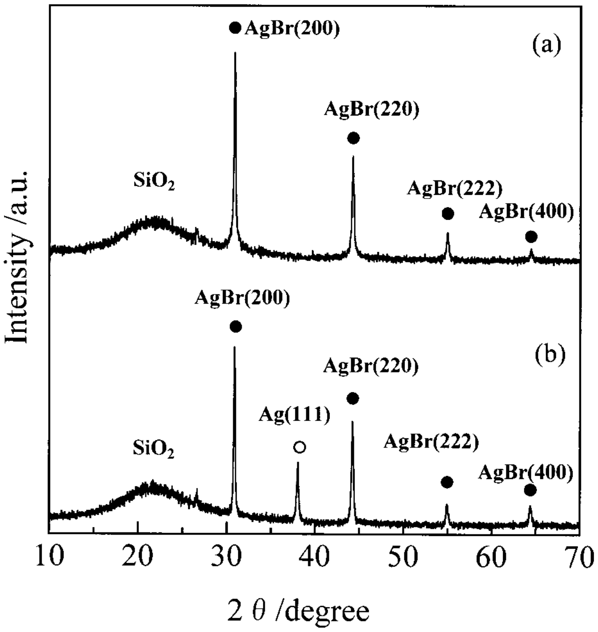

Figure 4. XRD spectra of AgBr/SiO$_2$ catalyst before (a) and after (b) UV illumination.

Previously, Chandrasekaran and Thomas[10] carried out the photolysis of water containing excess silver nitrate using the AgCl colloid solution. They found the formation of O_2 and the rapid breakdown of the colloid turned black as silver metals. This reaction is not a catalytic process because the colloids are eventually destroyed. Furthermore, the strong decrease in the O_2 yield was observed by the addition of a small amount of CH_3OH. It is noted that H_2 was not detected in their experiments. We also observed a similar effect in H_2 evolution. The H_2 evolution was lowered by the addition of Ag^+ ions to the CH_3OH/H_2O solution. Calzaferri et al.[11] measured the O_2 evolution over Ag^+ zeolite (not AgCl) from water containing Ag^+ ions under illumination, where Ag^+ ion was used for a scavenger of photoinduced electrons.

To elucidate the activity for H_2 formation, the catalyst was characterized by XRD after the photolysis of the CH_3OH/H_2O solution. Figure 4 shows XRD patterns before and after the photolysis. Initially, all sharp peaks were assigned to AgBr as described above, whereas after the reaction a new XRD peak corresponding to Ag[12] appeared together with the XRD peaks of AgBr and amorphous SiO$_2$. This means that the Ag formation occurred on AgBr at the early stage of the reaction, but AgBr was not destroyed under successive UV illumination. We consider the reason for the photoassisted H_2 production over AgBr/SiO$_2$ catalyst. The Ag^0 species is initially generated as described in the photographic theory, but the photodecomposition of AgBr is, in fact, inhibited even after UV illumination for 200 h, suggesting that the behavior of AgBr in the CH_3OH/H_2O solution might be somewhat different from the latent image formation. One explanation is that the formed Ag^0 species might act as the sites for the H_2 formation such as Pt on Pt/TiO$_2$ catalyst, and then further destruction of AgBr did not take place. The role of Ag species as the site for H_2 formation was reported by Sclafani et al.[13] using Ag/TiO$_2$, although the activity was less than that of Pt/TiO$_2$. In addition, alcohol radicals are known to generate hydrogen in the presence of silver colloids.[14] Consequently, although there is no evidence about whether the charge separation is smoothly performed in the presence of Ag species or Ag species catalyze the H_2 production from alcohol radicals formed by photoinduced hole, the high activity of AgBr/SiO$_2$ catalyst might be intimately related to the photogenerated Ag species. We also presume that the roles of SiO$_2$ support might assist the photocatalysis by the enhanced adsorption of methanol as proposed by Anderson and Bard[15] and might promote the high dispersion of AgBr crystallites. The stabilization mechanism of AgBr under UV illumination is not clear. Further experiments are necessary to understand the photocatalytic activity of AgBr on SiO$_2$ and behavior of methanol under UV irradiation. The results will be published elsewhere.

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