有効なスルフェド溶液からの水素生成についての研究

著者

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Effective Hydrogen Generation from the Hydrogen Sulfide Solution by using Stratified Type Photocatalyst

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Abstract. Stratified type photocatalyst with the extremely higher photocatalytic activities can be synthesized by using the chemical reaction between the Na2S solution and Cd(OH)2 precursors. This type of photocatalyst has the specific morphology which constructed by the nano-sized and capsule like formed structure, and the metal concentration was gradually changed in its wall. The “charge gradient” was formed at the metal sulfide and oxide/hydroxide junction in the wall, which favored for the separation of the photo excited electron-hole pair. Consequently, stratified type photocatalyst shows the high catalytic activity than the usual nano CdS particles. By the addition of sulfur compound into the bio reactor contained the sulfur reducing bacteria, the H2S gas concentration can increased to about 1000 times enlarge than the usual condition. Therefore, we can conclude that the enhancement of the H2S gas evolved from the bio reactor was successfully achievement, and we don’t need to afraid the shortage risk of H2S supply. These H2S gas concentration can enlarged to 80% by using A type zeorite. Especially, Ca-A type zeorite is considered as the suitable material.

Keywords: stratified type photocatalyst, hydrogen evolution, sulfur cycle

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INTRODUCTION

Recently, many researchers reported that natural energy should be utilized for the human life because of the depletion of fossil fuel and also the environmental problem. Among the various methods to utilizing the natural energy, photocatalytic decomposition of hydrogen sulfide (H2S) is considered as an efficient alternative route to produce new energy (hydrogen) compared with the splitting of water because of its low potential (H2S:0.298eV, H2:0.436eV). Moreover, decomposition of H2S by using solar energy and photocatalyst may gives us the candidate for the resolution of environmental problems, since quite large amounts of energy was consumed for the decomposition of H2S which evolved from the distillation of fossil fuel.

Among the various semiconductor materials, only the sulfide type photocatalyst can act stably in the H2S solution, while metallic and/or oxide type photocatalyst is sulfurized. Thus, sulfide type photocatalyst should be selected under the H2S condition.

Recently, Arai et. al reported that the synthesis of CdS nano-sized capsule which had the gradient Cd concentration in its wall, called as “stratified CdS nanoparticles”, and demonstrated that these materials showed the high photocatalytic activities for the decomposition of H2S[1]. Stratified CdS nanoparticles was synthesized by the reaction of Na2S and Cd(OH)2 or CdO nanoparticles[1]. In this meaning, photocatalytic decomposition of hydrogen sulfide (H2S) into hydrogen (H2) by using the stratified type photocatalyst is considered as efficient route for the conversion of natural energy (solar energy) into clean energy (H2). HS- ion was synthesized by dissolving the H2S as follows;

\[
\text{H}_2\text{S} \rightarrow \text{HS}^- + \text{H}^+
\]

Photodecomposition of HS- ion was obeyed to the following formula;

\[
2\text{HS}^- \rightarrow 2\text{H}^+ + \text{S}_2^{2-} + 2e^-
\]

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2
\]

From these formulas, it clearly observed that S2^{2-} ion is synthesized as the by-products.

FIGURE 1. schematic drawing the sulfur cycle system
So, if the effective conversion route from $S_2^{2-}$ ion into H$_2$S gas is developed, sulfur cycle for the new energy generation can be constructed. Figure 1 shows the schematic drawing the sulfur cycle system studies in this study. To construct this system, we should clear the six elemental factor mentioned below.

1) Development of the effective conversion route from $S_2^{2-}$ ion into H$_2$S gas by using the bio reactor.
2) Concentration of the H$_2$S gas from the bio generated gas containing the CH$_4$, CO$_2$, and ammonia.
Evolved gas from the bio reactor was contained the various gas. CH$_4$ gas can be separated easily, while CO$_2$ gas can not be separated from the H$_2$S gas by the traditional method since the nature of each gas is almost the same. In this system, NaOH solution was used in the photocatalytic reaction. If the CO$_2$ was contained in the H2S gas, NaOH was consumed during the reaction. Therefore, CO$_2$ should be removed from the H$_2$S gas.
3) Synthesis of the stratified type photocatalyst with very high photocatalytic activities.
4) Development of the concentration route of $S_2^{2-}$ ion dissolved in the water.
5) How to transfer the $S_2^{2-}$ ion collected in 4) to the bio reactor.
6) Synthesis of the film type photocatalyst by using the stratified type materials for the easy handling.

In this literature, our resent research on the elemental factor 1) to 3) will be reported.

DEVELOPMENT OF THE EFFECTIVE CONVERSION ROUTE FROM $S_2^{2-}$ ION INTO H$_2$S GAS BY USING THE BIO REACTOR

Experimental

400 ml of the bio reaction solution which contained the sulfur reducing bacteria, such as the thiobacillus, was introduced into the reaction vessel (500ml). 15 ml/day of the sludge, as the “food” for the bacteria, was introduced into the vessel. Same volume (15 ml) of the reacted solution was removed every day. After three weeks, 0.01 mol of sulfur or Na$_2$SO$_4$ was added with the sludge. Volume of the generated gas was measured by the flow meter, and collected to the gas bag. Concentration of the each gas species was analyzed.

Results and Discussion

Figure 2 shows the change in the concentration of H$_2$S, CH$_4$ and CO$_2$ gases in the bio reacted gas, before and after 0.01 mol sulfur addition. In usual case (when large volume of reaction vessel was used), concentration of H$_2$S, CH$_4$ and CO$_2$ was reported to c.a. 500 ppm, c.a. 60% and c.a. 40%, respectively. On the other hand, in this case, initial concentration of each gas was about 100 ppm (H$_2$S), c.a. 15 % (CH$_4$), and c.a. 25 % (CO$_2$), and the variation of each species was negligible. By the addition of sulfur in the system, the tendency, which H$_2$S gas and also CH$_4$ gas was increased while that of CO$_2$ was decreased, was clearly observed. Especially, the concentration of H$_2$S gas was suddenly increased by the addition of sulfur, and it reached c.a. 500 times larger than initial concentration. The concentration of H$_2$S gas was also increased by the addition of Na$_2$SO$_4$, nevertheless its concentration was gradually increased as compared with the case of sulfur addition.

Initial concentration of each gas was differed from the usual case’s concentration as mentioned above. Therefore, we considered that these results had some unreliability, possibly originated from the oxygen diffusion to the bio solution, since sulfur reducing bacteria was died in aerobic condition. However, it is true the fact that the concentration of H$_2$S was extremely enlarged by the addition of sulfur compound, until it can not be reached by using the usual system. More precise research of this bio reaction is now in progress, vigorously.
CONCENTRATION OF THE H2S GAS FROM THE BIO GENERATED GAS CONTAINING THE CH4, CO2, AND AMMONIA

Experimental

40 g of zeorite was introduced into the vessel. 3 cm of the glass beads layer was settled at the upper and the lower side of the zeorite layer for the gas diffusion. Three different types of zeorite, namely Ca-A type, Na-A type and K-A type zeorite, was used for the experiment. Original gases which contained the H2S, CO2 and N2 were settled in the gas bag. In the case 1, gas with the ratio of CO2 : N2 = 20 % : 80 % was pass through until CO2 was detected in the sampling gas bag. At the next step, pure N2 gas was introduced into the zeorite layer to remove the CO2 existed in dead volume area. Finally, gas with the ratio of H2S : N2 = 20 % : 80 % was pass through until H2S was detected in the sampling gas bag. In the case 2, sequence of the H2S contained gas flow and CO2 contained gas flow was inverted. Flow rate was adjusted to 6 L/h. The concentration of gases in the sampling gas bag was measured after passing through of 1.4 L original gas. After the measurement, gases in the gas bag were pumped out before next gas flow.

Results and Discussion

Figure 3 shows the total gases volume remained in the (a) Na-A type zeorite and (b) Ca-A type zeorite. Maximum capacity of the CO2 adsorption on the surface of (a) Na-A type zeorite and (b) Ca-A type zeorite was c.a 2.4 L and c.a 2.7 L, respectively. By introducing the H2S gas, capacity of the CO2 adsorption on these zeorite was decreased to c.a 1.1 L (Na-A type zeorite) and 0.5 L (Ca-A type zeorite). On the other hand, 2.2 L (Na-A type zeorite) and 3.5 L (Ca-A type zeorite) of H2S gas was adsorbed on its surface. The ratio of H2S gas adsorbed on the surface of zeorite was reached to c.a 65 % and c.a 87 %. Taking the gas composition of the bio reacted gas, which large amount of CO2 gas was contained, into consideration, the experimental condition of case 1 is similar to the real condition. Thus, it can be concluded that concentration of H2S gas generated from the bio reactor can be achieved by using A type zeorite, and Ca-A type zeorite is considered as the suitable material.

SYNTHESIS OF STRATIFIED TYPE PHOTOCATALYST WITH VERY HIGH PHOTOCATALYTIC ACTIVITIES

Experimental

Synthesis method of stratified CdS type photocatalyst is almost the same to that of ZnS type photocatalyst [1]. Briefly, first, the Cd(OH)2 precursor were treated in 0.1 M Na2S solutions. By this reaction, CdS layer of about few-10nm was synthesized on the surface of the hydroxide precursor. Then, the Cd(OH)2 core was removed by dissolving the 1M HCl solution. Finally, the surface of the catalyst was modified by Pt nanoparticles [2]. CdS particles synthesized by this method are called as “s-CdS”. For comparison, nanometer size CdS particles were synthesized in the liquid phase [3-5]. The surface of these particles was also treated with Pt. We refer to these CdS particles as “nano-CdS”.

Synthesized materials were analyzed by XRD, SEM, TEM and UV-Vis spectroscopy. Additional information about the morphology and metal ion distribution of the s-CdS were obtained from particles processed using FIB, and analyzed using EDX in a HR-TEM.

Photocatalytic Activity

Photocatalytic decomposition of H2S was obeyed to the following formula;

\[ \text{H}_2\text{S} \rightarrow \text{HS}^- + \text{H}^+ \quad (\text{dissolution of H}_2\text{S}) \]

\[ 2\text{HS}^- \rightarrow 2\text{H}^- + \text{S}_2^{2-} + 2e^- \]
2H⁺ + 2e⁻ → H₂

HS⁻ ion was also formed by dissolving the Na₂S in the basic aqueous solution (pH 13). Thus, photocatalytic reactivity of the synthesized materials could be evaluated by measuring the evolved amount of H₂ from Na₂S solution. 300mg of synthesized photocatalyst particle and 150ml of Na₂S reaction solution were put into the quartz reaction vessel, and then 5.0W UV-light was irradiated from the bottom of the vessel. Mercury lamp (WACOM Electric CO., LTD.; BMP-500D1) was used as the light source.

Results and Discussion

XRD results clearly demonstrated that Cd(OH)₂ (JCPDS# 40-0760 (monoclinic structure), 31-0228 (hexagonal structure)) and CdS (JCPDS# 10-0454 (cubic structure)) was co-existed in the synthesized materials. The peaks of CdS were broadened as same as in the case of stratified ZnS, nevertheless Cd(OH)₂ precursor has two crystal phase in this case. The reflection spectra of s-CdS suggested that the absorption began around 520nm.

HR-TEM micrograph of s-CdS (Fig.4) demonstrated that s-CdS has nano-sized and capsule like formed structure as same in the case of stratified ZnS particles. Therefore, it considered that stratified CdS photocatalyst can also be successfully synthesized by this method.

FIGURE 4. HR-TEM micrograph of s-CdS

Figure 5 shows the photocatalytic activity (evolved amount of hydrogen) of the stratified CdS and also the nano-CdS particles. The hydrogen generation rate for Pt-deposited nano-CdS particles was almost equal to the highest value reported in the literature [6]. On the other hand, its rate of the stratified CdS photocatalyst was about ten times higher than the reported value, and was determined to be about 200 ml/h for 32 Wh of input light energy. The quantum efficiency under the above condition was reached to 15% on the average for light beam up to 520nm.

FIGURE 5. Photocatalytic activity (evolved amount of hydrogen) of the stratified CdS and also the nano-CdS particles

When the light irradiation time exceeded two hours, the hydrogen evolution rate of the stratified CdS photocatalyst becomes decrease, and it was stopped finally. In this time, mole of generated H₂ gas was almost the half mole of HS⁻ ion added (2HS⁻ → H₂↑ + S₂²⁻). By the replacement of the solution in the reaction cell with fresh Na₂S solution, the hydrogen evolution rate was recovered to the previous highest value. Thus, the photocatalytic activity of stratified CdS could be attributed to the consumption of HS⁻ ions, and it can be said that stratified CdS photocatalyst has the long life time.

CONCLUSION

By the addition of sulfur compound into the bio reactor contained the sulfur reducing bacteria, the H₂S gas concentration can increased to about 1000 times enlarge than the usual condition. Therefore, we can conclude that the enhancement of the H₂S gas evolved from the bio reactor was successfully achievement, and we don’t need to afraid the shortage risk of H₂S supply. These H₂S gas concentration can enlarged to 80% by using A type zeorite. Especially, Ca-A type zeorite is considered as the suitable material.

Stratified type photocatalyst with the extremely higher photocatalytic activities can be synthesized by using the chemical reaction between the Na₂S solution and Cd(OH)₂ precursors. This type of photocatalyst
has the specific morphology which constructed by the nano-sized and capsule like formed structure, and the metal concentration was gradually changed in its wall. The “charge gradient” was formed at the metal sulfide and oxide/hydroxide junction in the wall, which favored for the separation of the photo excited electron-hole pair. Consequently, stratified type photocatalyst shows the high catalytic activity than the usual nano CdS particles.

REFERENCES