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Hydrogen Production from Water by Using Hydrogen Sulfide as Reducing Agent in Hydrothermal Reactions

Cuixiang Ma[1], Fangming Jin[1]*, Guangyi Zhang[1], Xu Zeng[1], Jianglin Cao[1], Takeo Mogi[2], Atsushi Kishita[2] and Heiji Enomoto[2]

[1]State Key Laboratory of Pollution Control and Resources Reuse, College of Environmental Science and Engineering,

Tongji University, Shanghai, China

[2]Graduate School of Environmental Studies, Tohoku University, Sendai, Japan

fmjin@mail.tongji.edu.cn*

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ABSTRACT

The aim of this work is to investigate the hydrogen generation from water using H_2S as a reducer in hydrothermal reactions. The effects of reaction temperature, reaction time and initial pH values of reaction solution on the production of hydrogen from water were studied. The experimental results showed that hydrogen could be produced from water only when the reaction temperature was beyond 200 ^oC. Moreover, the hydrogen production strongly depended on the initial pH values of the solution. Under strong alkaline conditions the hydrogen production from water was much higher than that under acidity or weak alkaline conditions. The possible mechanism of hydrogen production was discussed.

1. INTRODUCTION

Our current energy infrastructure is dominated by fossil fuels which are being depleted. Considerable efforts are always under way to search for an alternative to fossil fuels. Hydrogen is considered as a nonpolluting, efficient, inexhaustible energy carrier to alternate fossil fuels for the future. When hydrogen combines with oxygen, only water is formed as the reaction product. Recently, the hydrogen production from water has attracted much more attention than that from the other primary sources, such as natural gas, heavy oil, methanol, biomass, wastes and coal, etc (Manuela and Michele (2003), Chang and Laia (2008), Guo and Lu (2007), Yukihiro and Ki (2008)).

High-temperature water (HTW) is a promising new medium due to its environmentally benign nature and feasibility in the adjustment of solvent characters (Naoko and Phillip (2002)). The hydrogen bonding in water becomes weaker and less persistent with increasing temperature and decreasing density in HTW. Furthermore, HTW exhibits an increasing solubility toward organic compounds. Individual water molecules can actively participate in the reaction as reactants and/or as catalysts.

It is well known that H_2S is a strong reducer. Moreover dissolved sulfide was detected in hot spring waters (Xu and Schoonen (1998)). Our past studies on hydrothermal treatment of sulfur-containing rubber showed that H_2S and hydrogen could be produced. However, the conversion mechanism of hydrogen production in hydrothermal reaction is not yet fully understood. It is mostly likely that hydrogen is produced from HTW because H_2S acts as a reducer in HTW due to its strong reduction property. The enormous heat inside the earth can be used continuously for heating and electricity generation. Worldwide, geothermal power covers only a rough 0.5% of the total primary energy supply. However, its potential is nearly inexhaustible. Expert calculations suggest that theoretically more than ten times the global energy demand of today could be generated by geothermal power every year (Yorozu and Hirano (1987), Young (1989)).

Therefore, hydrogen from water might be generated with H_2S acting as a reducer by utilizing low environmental burden heat source such as geothermal energy for the hydrothermal reaction. The aim of this work is to investigate that hydrogen generates from water using H_2S as reducer in hydrothermal reaction.

2. EXPERIMENT SECTION

2.1 Experiment Materials

Due to the toxicity of H_2S, $Na_2S·9H_2O$ was selected as test material to replace H_2S. $Na_2S·9H_2O$ (99.99%) were purchasing from Sigma-Aldrich company. Hydrochloric acid and sodium hydroxide (AR) were used to adjust the initial pH values of the Na_2S aqueous solution. Hydrochloric acid and sodium hydroxide were obtained from Sino-pharm Chemical Reagent Co., Ltd.

2.2 Experiment Procedure

The experiments were conducted using a batch reactor made of Hastelloy C-276 with an internal volume of 42 ml. The batch reactor was connected with the gas-collection equipment. The typical procedure was as follows: the desired amount of $Na_2S·9H_2O$ and water were added to the batch reactor and then sealed. The reactor was put into an induced heating furnace and then heated to a desired temperature with an increasing rate of 40 ^oC / min. The induced heating furnace was swayed with a frequency of 20 times / min during experiments. After a desired reaction time, the reactor was removed from the induced heating furnace and cooled by the electric fan. All experiments were performed with degassed water and the reactor was purged with nitrogen. The reaction time was defined as the time during that reactor was kept at the desired temperature. Experimental conditions for producing hydrogen are as follows: reaction temperature 200-330 ^oC, reaction time 0.5-8 h, and water fill 36 %.

2.3 Sample Analysis

After reaction, liquid and gas samples were collected for analyses. The gas samples were analyzed by an Angilent 6890 gas chromatographs with thermal conductivity detection (GC-TCD) equipped with molecular sieve 5A columns. The liquid samples were filtered using a syringe filter with 0.45-μm filter film. The separation of sulfur anions in aqueous solution were analyzed by an Agilent

Capillary Electrophoresis (CE) system equipped with a UV-Vis absorbance diode array detector (DAD). The separation of sulfur species were achieved with indirect UV detection at two different wavelengths: 214 nm with reference at 372 nm.

3. RESULTS AND DISCUSSION

3.1 Effects of Reaction Temperature and Reaction Time on Hydrogen Production from Water

To examine the production of hydrogen from water with H_2S as a reducer, hydrothermal experiments were performed with 3 mmol $Na_2S{\cdot}9H_2O$ (0.2 mol/L) by varying the reaction temperature and reaction time. Fig. 1 gives the production of hydrogen at varying temperatures from 200 ^oC to 330 ^oC and different reaction times.

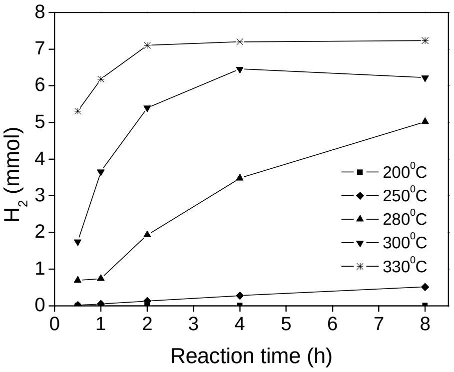

Figure 1: Hydrogen Production at different temperatures and times (Na_2S 3 mmol, 15 ml solution).

As shown in Fig. 1, almost no hydrogen was produced at 200 ^oC. To further confirm whether hydrogen was not produced from water at 200 ^oC, hydrothermal experiment was conducted with 6 mmol $Na_2S{\cdot}9H_2O$ (0.4 mol/L) at 200 ^oC for a long reaction time of 12 h. The result showed that no hydrogen was produced either. These experimental results indicated that the energy from the reaction temperature of 200 ^oC could not offer sufficient energy to break the H-bond in the water with HS^- as reducing agent.

From Fig. 1, it also can be seen that at the same reaction time the production of hydrogen increased markedly as the temperature increased. The results showed that a higher temperature was favored to produce hydrogen from water by using H_2S as the reducing agent.

In addition, the production of hydrogen slightly increased at 250 ^oC with increase the reaction time. The significant increase in hydrogen production at 300 ^oC was observed as the reaction time increased. And when the temperature further increased, the maximum yield of hydrogen was rapidly obtained as the reaction time increased. These results showed that hydrogen can be produced at the temperature over 200 ^oC and a higher temperature was favored to produce hydrogen from water by using H_2S as the reducing agent. At higher temperature, the maximum yield of hydrogen was easier to obtain as the reaction time increased.

Considering supplying the energy to elevate the reaction temperature and a large quantity of hydrogen was produced at 300 ^oC, the temperature of 300 ^oC was selected to examine the other effect on the production of hydrogen from water.

3.2 Effect of the Initial pH of the Solution on the Production of Hydrogen from Water

Hydrogen sulfide is a weak diprotic acid and there can exist in three chemical forms in solution, H_2S, HS^-, and S^{2-} ions. The solution pH determines the distribution of these reduced sulfur species and is the predominant solution variable.

It is generally known that the ionizations of H_2S in water are carried out by the follow two equilibriums:

$$H_2S^- \xleftrightarrow[k_1]{} H^+ + HS^- \tag{1}$$

$$HS^- \xleftrightarrow[k_2]{} H^+ + S^{2-} \tag{2}$$

the ionization constants (pKa) for eq. (1) and eq. (2) are 7.02 and 14, respectively, at ambient temperature. The distribution of dissociation species of H_2S at ambient temperature is shown in Fig. 2.

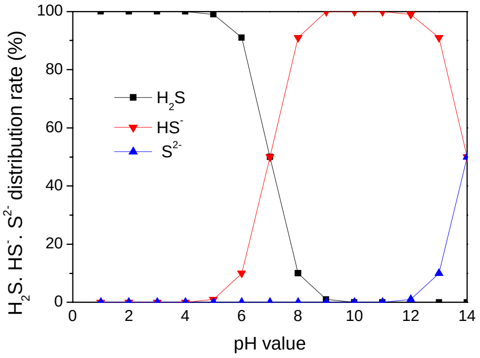

Figure 2: The calculated distribution rate of H_2S dissociation species.

Although the distribution of dissociation species of H_2S in high temperature and pressure water has been not yet known well, it has been reported that the ionization constant of H_2S was about 8 and that of HS^- was slight less than 14 in hydrothermal system, suggesting that the ionization constants are almost the same at ambient temperature and high temperature (Ellis and Giggenbach 1971). Thus, in the pH range from 8 to 11, the hydrosulfide ion (HS^-) is the primary species, while the hydrogen sulfide molecule [H_2S(aq)] becomes the predominant reduced sulfur species below pH 7. The pH value of the liquid reaction sample was detected by pH meter. It was found that the solution pH increased from 13 to 13.7 with 3 mmol Na_2S at 300 ^oC for 1 h in the hydrothermal reaction. It might be due to the formation of OH^- as shown in eq. (3)

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \tag{3}$$

Therefore, the production of hydrogen might be effected by the distribution of H_2S in the hydrothermal reactions. Further experiments were performed to examine the effect of the solution initial pH on the production of hydrogen from water.

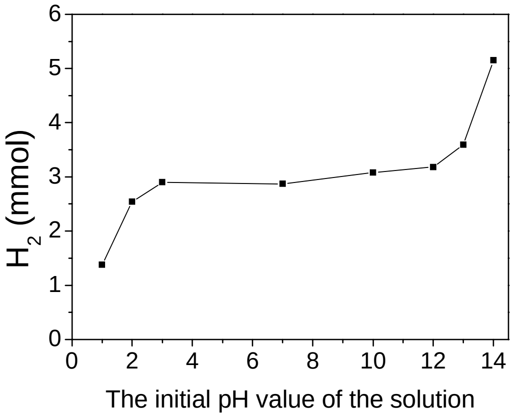

Figure 3: **Effect of initial pH of the solution on the yield of hydrogen (Na_2S 3 mmol, temp. 300 °C, time 1h, 15 ml solution).**

Fig. 3 shows the production of hydrogen from water with 3 mmol Na_2S on the dependent of the initial pH from 1 to 14 at 300 °C for 1 h. HCl and NaOH were used to adjust the initial pH of the Na_2S aqueous solution. With increasing the initial pH, the yield of hydrogen was increased. The yield of hydrogen was 1.38 mmol when the initial pH was 1. In the pH rang from 2 to 12, the yield of hydrogen was almost not changed. While increasing the pH from 13 to 14, the yield of hydrogen was significantly increased from 3.59 to 5.15 mmol. The results indicated that the production of hydrogen from water was favored at strong alkaline conditions.

3.3 Effect of the Initial Amount of Na_2S on Production of Hydrogen

As mentioned above, the hydrogen production might be attributed to the oxidation of HS^- into $S_2O_3^{2-}$ and SO_3^{2-}. If so, the amount of hydrogen should increase with the increase of H_2S amount. Fig. 4 gives the effect of Na_2S amount on the production of hydrogen at 300 °C for 4 h. As expected, the amount of hydrogen increased linearly with the increase of Na_2S amount as seen in Fig. 4. The ratio of hydrogen to Na_2S was about in range from 2.1 to 2.2 with the different amount of Na_2S. These results indicated that the production of hydrogen was related with the amount of HS^- in the initial solutions.

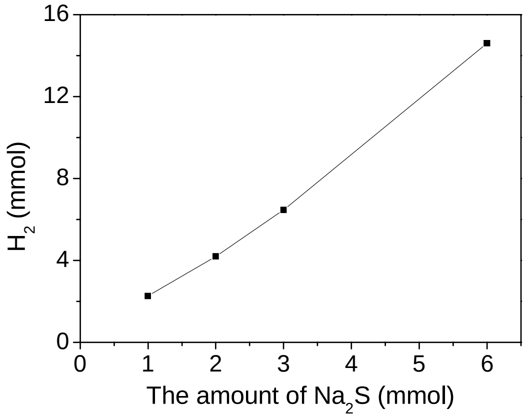

Figure 4: Effect of the amount of Na_2S on the production of hydrogen from water (Na_2S 1, 2, 3, 6 mmol, temp. 300 °C, time 4 h, 15 ml solution).

3.4 The mechanism of the Production of Hydrogen with H_2S as reducing agent

The liquid sample was analyzed by CE to detect the sulfur-bearing compounds after the hydrothermal reactions. Fig. 5 shows the CE chromatogram of the liquid sample with 3 mmol Na_2S at 300 °C for 1h. As shown in Fig. 5, in addition to HS^- ions, $S_2O_3^{2-}$, SO_3^{2-}, and SO_4^{2-} ions were also detected. It indicated that HS^- ions were oxidized into $S_2O_3^{2-}$, SO_3^{2-}, and SO_4^{2-} ions during the hydrothermal process.

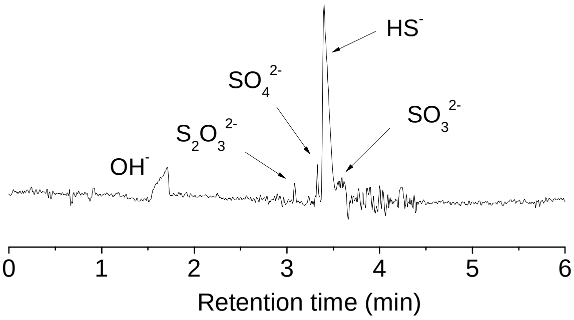

Figure 5: CE chromatogram of the liquid sample (Na_2S 3 mmol, temp. 300 °C, time 1h, 15 ml solution).

With the reaction time increased, the amount of HS^- ions was decreased while the amount of $S_2O_3^{2-}$, SO_3^{2-}, and SO_4^{2-} ions were increased (Date not shown). The results confirmed that HS^- ions were oxidized into $S_2O_3^{2-}$, SO_3^{2-}, and SO_4^{2-} ions when the hydrogen was produced from the water. Consequently, the mechanism of hydrogen production might be proposed as follows:

$$2HS^- - 2e \rightarrow \frac{1}{2}S_2O_3^{2-} \tag{4}$$

$$\frac{1}{2}S_2O_3^{2-} - 2e \rightarrow SO_3^{2-} \tag{5}$$

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \tag{6}$$

According to the proposed mechanism, when HS^- ions were completely converted into $S_2O_3^{2-}$ ions, the ratio of the yield of hydrogen to the initial amount of Na_2S should be 2 in theory. While the production of hydrogen was not increased with enough reaction time, the ratio of hydrogen to the mount of Na_2S was about in range from 2.1 to 2.2 in the experiment (see Fig. 3). The results indicated that $S_2O_3^{2-}$ ions convert into SO_3^{2-} and SO_4^{2-} ions at the same time hydrogen was produced from water. To further confirm whether hydrogen did produce from water with the addition of $S_2O_3^{2-}$ ions, hydrothermal experiment was conducted with 1.5 mmol $Na_2S_2O_3{\cdot}5H_2O$ (0.1 mol/L) at 300 °C for 4 h. The result showed that a small amount of hydrogen was produced.

4. CONCLUSIONS

Hydrogen could be produced from water only when the reaction temperature was beyond 200 °C. The production of hydrogen in strong alkaline conditions was favored than in the acidity or weak alkaline conditions. The possible mechanism of hydrogen production was proposed that hydrogen sulfide were oxidized into $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-} ions, meanwhile, hydrogen was produced from water in hydrothermal reaction.

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