CHEMICAL PROCESSES FOR GENERATION OF HYDROGEN BY “GEOREACTOR”

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ABSTRACT

Production of hydrogen by using geothermal energy was investigated. “Georeactor” is one of advanced direct use for chemical reactions to produce hydrogen and material conversion. We have to select adequate chemical processes for generation of hydrogen for applying “Gepreactor”. Hydrogen sulfide (H_2S, HS^- and S^{2-}) has great potential to produce hydrogen under hydrothermal condition, however, oxidized sulfur species such as SO_4^{2-} and $S_2O_3^{2-}$ were produced as by-product of generation of hydrogen. Some of organic compounds and urea had possibilities to reduce oxidized sulfur species into reduced sulfur species to reproduce hydrogen. We carried out hydrothermal experiments involving two reaction steps which were production of hydrogen and reduction of sulfur oxidized species. We can obtain over 40% conversion rate to produce hydrogen under hydrothermal condition by using the lab-scale georeactor.

Keywords: geothermal direct use, chemical reaction, georeactor, hydrogen, sulfur cycle, hydrothermal reaction

1. INTRODUCTION

After East Japan Great Earthquake and Fukushima nuclear accident, geothermal energy has been reassessed as one of main renewable energy resources. Geothermal resources in Japan have been chiefly developed for electric power generation, with relatively small amount of additional direct utilization of geothermal energy. It is also possible to utilize the geosphere environment for material processing and energy conversion, due to its high temperature-pressure conditions, which is an alternative and advanced direct use of geothermal energy. Many chemical reactions for producing hydrogen have been proposed, however, temperature and pressure conditions under developed geothermal environment are limited. We have to find and select adequate chemical processes for generation of hydrogen by using “Georector” under geothermal conditions (Satiani et al., 2011 and Zhang et al., 2011).

Fig. 1 shows conceptual model of sulfur cycle for hydrogen production using solar, geothermal energies and biochemical reactions. In order to design a complete closed loop of hydrogen production system, reacted sulfide ions have to be converted into photocatalysis-active hydrogen sulfide ions.

Georeactor, which is a kind of chemical reactor using geothermal energy, can be applicable to hydrogen generator couples with solar energy (Tsuchiya *et al.*, 2003, 2008) . Takahashi *et al.* (1987) showed first idea of “georector” (actually they proposed Geothermal reactor), After modifying their idea, Fig. 2 shows several types of georeactor. Firstly, a tube type chemical reactor, which comprises either double and/or multiple tubes with extremely high aspect ratio, which is similar to the single well type. Secondly, a steam (and hot water) generator that circulates cold water through an inner (or outer) tube. In the case of material processing type system, starting materials are supplied through the tube, which

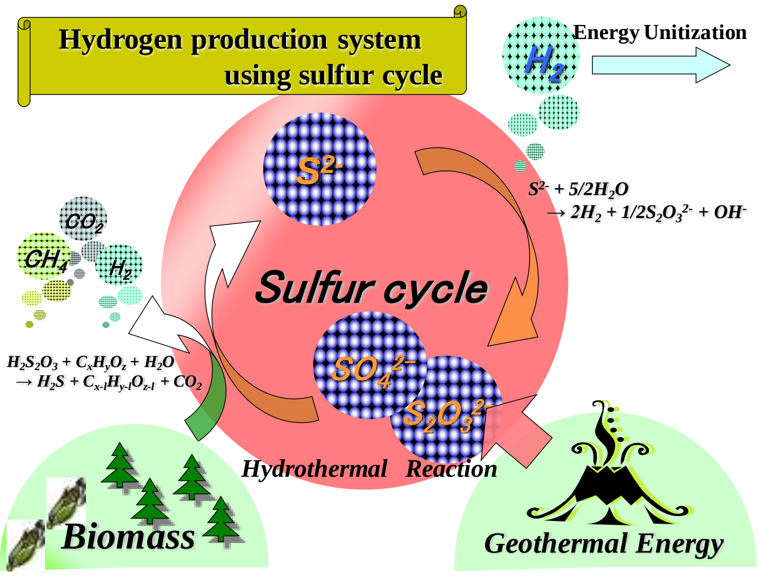

Fig. 1 Sulfur Cycle and Hydrogen production using solar, geothermal energies and biochemical reactions.

interact at pre-determined temperature-pressure conditions. Reacted materials (e.g. slurry of useful materials and/or gaseous components) can be recovered from the tube reactor. If the chemical process requires several raw materials, then multiple tubes may be utilized. In this paper, we describe chemical processes in the georeactor, which can be used to promote sulfur reduction for hydrogen generation. Earth conscious hydrogen generation process, which is sustainable and environmentally friendly hydrogen supply system.

2. CHEMICAL PROCESSS

Self-oxidation and reduction of sulfur

Sulfur is complex element, due to the behavior of many kinds of sulfide and sulfate compounds. In particular, the following self-oxidation and reduction is well known to represent chemical sulfur-water interaction (Tsuchiya and Watanabe, 2011):

$$4S + 4H_2O \rightarrow 3H_2S + H_2SO_4 \qquad (1)$$

Sulfur- water interaction

$$2\,HS^{-} \rightarrow H_2 + 2\,S^{2-} \qquad (2)$$

Due to chemical reaction (1) and (2), one of the reacted products from elemental sulfur is sulfate ions (SO_4^{2-}), whilst the reduction of H_2S species dissociates to HS^- and S^{2-}. Oxidation and reduction reactions may occur simultaneously in solution. Reduction products, H_2S or HS^- are useful for hydrogen production, and we examined the chemical behavior of sulfur, and corresponding self-oxidation/reduction reactions over a wide range of chemical conditions.

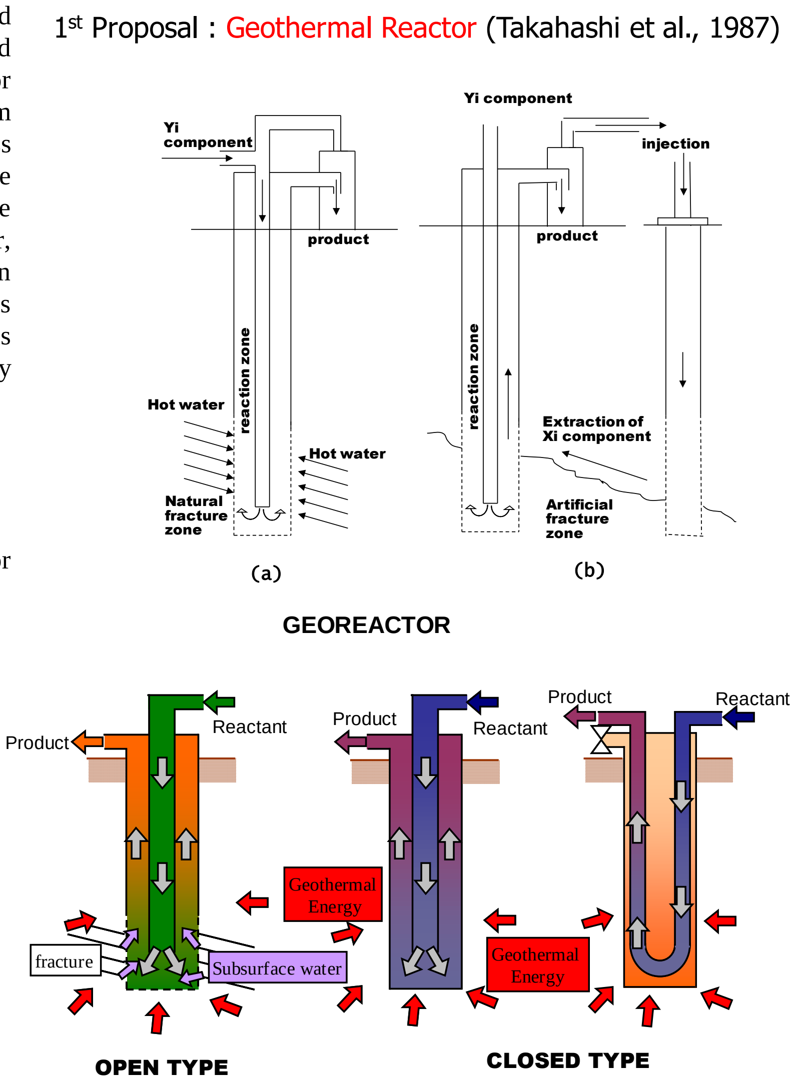

Fig.2 First proposal of geothermal reactor and conceptual model of several types of “Georeactor”.

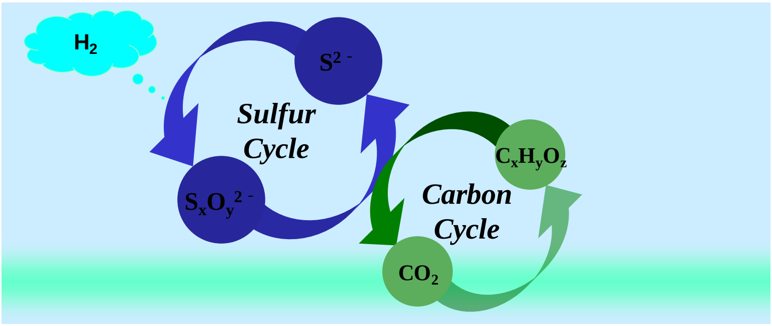

Fig.3 Conceptual reaction model including sulfur cycle and carbon (carbon dioxide) cycle.

Sulfur-water-organic compound interaction

We studied sulfur-water-organic matter interaction, and particularly on the effective utilization of waste elemental sulfur, which can be converted to a useful sulfur resource for hydrogen production. The self-redox reactions of sulfur is occurred inevitably during hydrogen generation in chemical cycle of sulfur, and alternative reducers are required to sulfur hydrothermal reaction for sustainable hydrogen generation system. Reduction products of elemental sulfur, H_2S (HS^- and S^{2-}), is necessary for hydrogen production system, but other oxidized products, ex. H_2SO_4 and $H_2S_2O_3$, are useless species throughout hydrogen production system.

In this study, organic matters are focused on as reducers of sulfur, which is ideally represented by the following formula:

$$S + H_2O + C_xH_yO_z \rightarrow H_2S + C_aH_bO_c + CO_2 \quad (3)$$

Here, oxidized organic matters were produced as waste products accompanied with CO_2, which are potentially re-converted to initial organic matters using the georeactor. Fig. 3 shows conceptual reaction model including sulfur cycle and carbon (carbon dioxide) cycle.

3. EXPERIMENTAL

Batch type experiments:

reduction species without pH shift to acidic condition. Teflon autoclave which capacity was 28 ml and hastelloy autoclave which capacity was 40 ml were employed for hydrothermal experiment. The teflon autoclave was used for experiments under oxygen-existed conditions and the hastelloy autoclave was used for experiments under oxygen-free conditions. Pressure valve for air collection was installed in the seal corn of hastelloy autoclave. Air in the autoclave was replaced by nitrogen gas prior to the experiment under oxygen-free condition.

The experiment was carried out after adjusting pressure at 0.2 MPa with nitrogen gas. A high temperature dry oven with a rotation shaft for stirring autoclave was used to heat autoclaves. Reaction temperature was 200°C, and duration of reaction was 2, 4, 6, 8 and 12 hours.

Starting materials were elemental sulfur or sodium thiosulfate, determined amount of organic matters and purified water or 30% alcohol solution. Whole solution volume was adjusted 15ml. Many types of organic compounds were used for experiments under oxygen-existed conditions. Formic acid, glycerin, methanol, ethylene glycol, ethanol, sodium stearate, sodium citrate, urea, glucose, stearic acid and phenol were used for the experiments as starting organic materials.

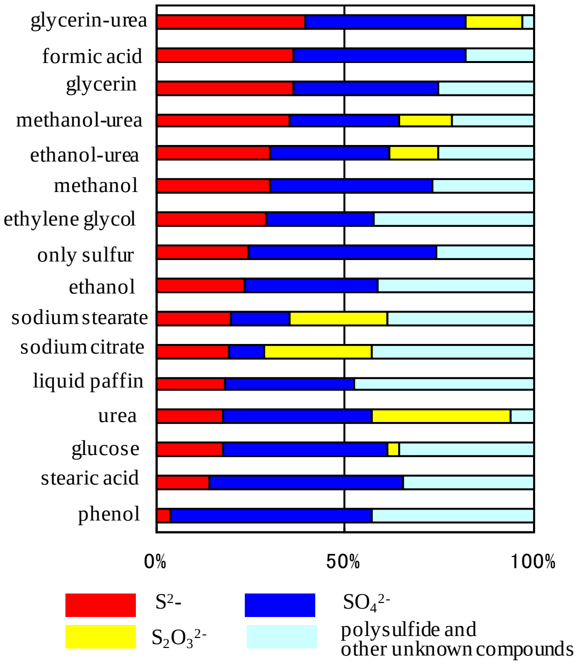

Fig. 4 Mass balance of sulfur-water and organic compounds after hydrothermal reactions. Reaction duration and initial pH are 12 hours and pH 6.8

Ion chromatography with UV spectrum and electric conductivity detector were employed to determine the quantities of S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, and SO_4^{2-}. In the experiment using the hastelloy autoclave the quantities of CO_2 gas and H_2S gas were determined by gas chromatography.

Flow through experiments:

Based on experimental results for searching relevant reagent to reduce thiosulfuric acid, hydrothermal experiments using a flow through type autoclave were carried out to combine dual reaction steps. Experimental apparatus as shown in Fig. 6. One reaction was reduction of thiosulfuric ions mixed with relevant organic compound (upper reaction tube), and the other was production of hydrogen (lower reaction tube) Temperatures of the lower reaction tube and upper one were 300°C and 200°C, respectively. Starting material was $Na_2S \cdot 9H_2O$ (50 mmol/l), and input 1-propanol (100%) between the lower and upper reaction tubes. Flow rate for both reaction tubes was 0.1 ml/min. Reaction time of the lower reaction tube and upper one were 330 min and 190 min. Additionally, long elapsed time for reduction of thiosulfuric acid in the upper reaction tube was 16 h and 60 h. Pressure was 10 MPa for both reaction tubes in any experimental conditions.

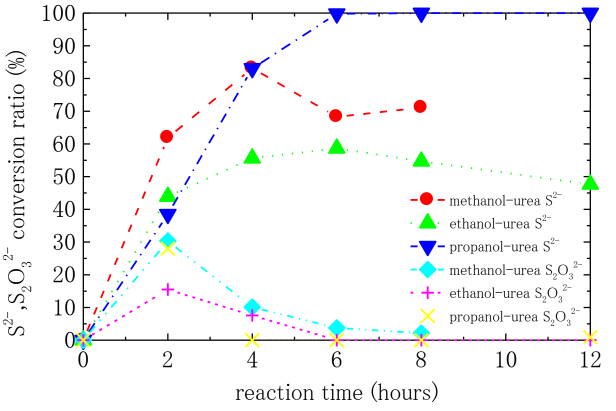

Fig. 5 Conversion ration of S into S^{2-} could be obtained by using propanol and urea. In this process, formed $S_2O_3^{2-}$

4. RESULTS AND DISCUSSION

Batch type experiments:

Fig. 4 shows mass balance of sulfur compounds after 12-hour reactions. Starting materials were elemental sulfur, organic material and purified water. Alcohols and acetic acid shows high yields of S^{2-}, which reveals all S(-II) species such as H_2S , HS andS^{2-}. Alcohol compounds with urea tend to promote sulfur reduction.

On the other hand, organic matters containing benzene ring and/or compounds of big molecular weight show low yield for reduction of sulfur. Urea only itself shows low yield of S^{2-} and promotes the formation of $S_2O_3^{2-}$. But it shows high conversion rate from elemental sulfur into detected sulfur compounds. Hydrolysis of urea represented following formula;

$$(NH_2)_2CO + 3H_2O \rightarrow CO_2 + 2NH_4^+ + 2OH^- \quad (4)$$

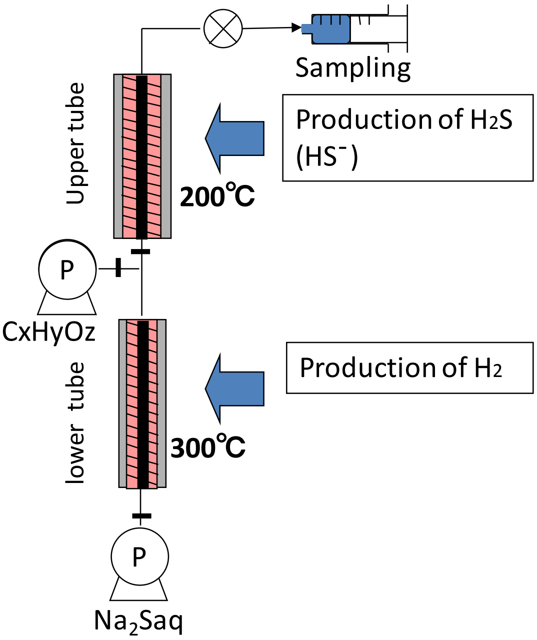

Fig. 6 Flow through hydrothermal experiment involving production of hydrogen (lower tube) and reduction of oxidized sulfur species (upper tube)

Urea is suitable for keeping pH of reacted solution in weak alkaline condition. Fig. 5 shows conversion ratio of elemental sulfur into S^{2-} by the experiments of sulfur hydrothermal reaction with alcohol and urea under oxygen-free condition. Duration of reaction was 2 to 8 hours. Starting materials were elemental sulfur, urea and 30% alcohol solution. Experiments of methanol compound with urea and ethanol compound with urea show high S^{2-} yields (80% and 60%). Complete conversion (100 % yield) from elemental sulfur into S^{2-} could be obtained by using propanol and urea. Although the molecular weight is methanol < ethanol < propanol, the yields of S^{2-} were ethanol < methanol < propanol. A slight amount of gray precipitation was observed on inner wall of autoclaves after the experiments of sulfur and ethanol and urea. It is considered as elemental sulfur or formed S^{2-} reacted with the inner wall. $S_2O_3^{2-}$ was formed by the hydrothermal reactions of sulfur with alcohol and urea. Yields of $S_2O_3^{2-}$ were maximized after 2-hour reaction and the formed $S_2O_3^{2-}$was decreased with elapsed time. To investigate the phenomenon of decreasing the formed $S_2O_3^{2-}$ the hydrothermal experiments using $S_2O_3^{2-}$ as a starting material were carried out. Duration of reaction was 2 to 8 hours. Starting materials were sodium thiosulfate, urea and 30% alcohol solution. The amounts of starting organic materials were equal to the experiments shown in Fig. 4. $S_2O_3^{2-}$ was mainly converted to S^{2-} by the solution containing propanol and urea. According to these experimental results, following reaction schemes could be considered in the hydrothermal reaction of sulfur, propanol and urea (Fig. 4).

$$4S + 3H_2O \rightarrow S_2O_3^{2-} + 2HS^- + 4H^+ \quad (5)$$

$$9S + C_3H_7OH + 5H_2O \rightarrow 9S^{2-} + 3CO_2 + 18H^+ \quad (6)$$

$$9S_2O_3^{2-} + 4C_3H_2OH \rightarrow 18S^{2-} + 12CO_2 + 18H^+ + 7H_2O \quad (7)$$

Weak alkaline condition of the reacted solution was generated and maintained by hydrolysis of urea (reaction (4)), and then reactions (5), (6), and (7) were occurred. Alcohol compounds had great role for reduction of sulfur, and hydrolysis of urea kept weak alkaline pH condition of the solution throughout hydrothermal reaction.

Flow through experiments:

Chemical reaction in the lower reaction tube for production of hydrogen was described as follows;

$$S^{2-} + 5/2H_2O \rightarrow 1/2S_2O_3^{2-} + 2H_2 + OH^- . \quad (8)$$

After production of hydrogen, by-product as oxidized species was thiosulfuric ion ($S_2O_3^{2-}$). In the upper reaction tube thiosulfuric ion was converted into reduced sulfur species for production of hydrogen such as HS^- and H_2S with organic compound, and theoretical chemical reaction was described as follows;

$$S_2O_3^{2-} + C_xH_yO_z + H_2O \rightarrow 2HS^- + C_{x-1}H_{y-1}O_{z-1} + CO_2 \quad (9)$$

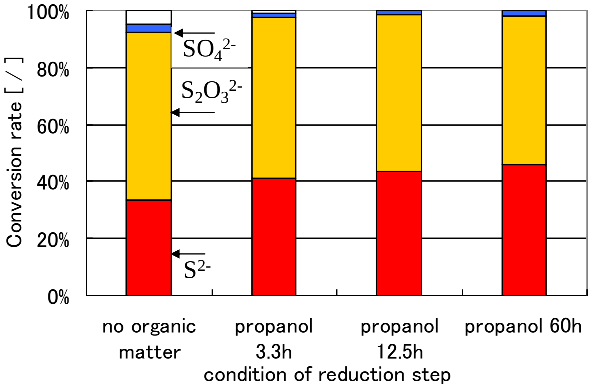

Fig. 7 Conversion rate of sulfur species after hydrothermal reactions.

According to the batch type experiments shown in Fig. 4, propanol had great potential to reduce thiosulfuric ion. Here, organic compound described in reaction (9) was 1-propanol (propyl alcohol, C_3H_8O).
Fig. 7 shows conversion rate of sulfur species. Thiosulfuric ion was still remained in the reaction tube, however, we can obtain over 40% of the conversion rate for S^{2-}. Those experimental results indicate that coupled reactions of production of hydrogen and reduction of thiosulfuric acid under hydrothermal condition were possible.

5. CONCLUSIONS

We carried out the experiments of hydrothermal reaction of sulfur with many types of organic matters. The results show alcohols promote sulfur reduction and urea keep pH of solution as alkaline condition, and then promote formation of $S_2O_3^{2-}$.The yields of S^{2-} in the reaction of ethanol compound with urea and methanol compound with urea were 60% and 80% respectively. Complete conversion (100 % yield) from elemental sulfur into S^{2-} could be obtained by using propanol and urea. In this process, formed $S_2O_3^{2-}$ was converted to S^{2-}.
Based on experimental results by using the batch type autoclave, we carried out hydrothermal reaction using tube reactor for flow though reactions. Coupled reactions for production of hydrogen and consequent reaction for reduction of thiosulfuric acid under hydrothermal condition has possible potential to create sustainable sulfur cycle for hydrogen production system using hydrothermal reaction. Additional experimental works are required to increase conversion rate, however, this chemical process is one of the advanced direct use of geothermal energy for sustainable production of hydrogen.
At a moment, there is no practical “Georector” system in the world. Geothermal energy has great potential as heat source. We have to investigate not only electric generation but also advanced direct use of geothermal power.

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