J Mater Sci (2008) 43:2115–2122
DOI 10.1007/s10853-007-2007-x

Sustainable hydrogen production system with sulfur–water–organic materials by hydrothermal reaction

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Received: 16 November 2006 / Accepted: 20 July 2007 / Published online: 9 October 2007

Abstract Engineered process for hydrogen generation from hydrogen sulfide ions in aqueous solution using solar energy with photocatalysis has been established. In order to design a complete closed loop of hydrogen production system, reacted sulfide ions have to be reduced to photocatalysis-active hydrogen sulfide ion. We focused on hydrothermal reaction of sulfur for reducing the reacted sulfide ions. But the oxidized sulfur species are occurred inevitably by the reaction. Thus alternative reducers are required to sulfur hydrothermal reaction for a complete closed loop of hydrogen production system. We studied sulfur–water–organic materials interaction, and particularly on the effective utilization of waste elemental sulfur. In this study, hydrothermal experiments of sulfur, water urea, and/or alcohols were carried out under atmospheric constituent condition and hypoxic condition at 200 °C. Experimental results show that maintaining solution in weak alkaline condition is important and alcohol compounds had a great role for reduction of sulfur. Elemental sulfur was completely reduced to hydrogen sulfide by the hydrothermal reaction of sulfur with urea and propanol under hypoxic condition. Those results indicate that it is possible to create sustainable sulfur cycle for hydrogen production system using hydrothermal reaction with organic compounds.

Introduction

Hydrogen is one of ultimate clean energy, being future main energy resources, however, hydrogen is secondary energy resource. Consequently the current production method of hydrogen is reformulation of fossil fuel. Huge energies were required to convert organic material into hydrogen by this method. The simplest formation chemical reaction of hydrogen is decomposition of water (H_2O).

Chemical processes for hydrogen generation by solar energy have been investigated using photocatalysis and pure water, however, process efficiency and conversion rate of hydrogen from water is not high. Additionally, the practical design of the system has difficulties due to low cost performance issues.

Recently new photocatalysis chemical process for hydrogen generation has been studied for aquatic solutions, using advanced nano-technology [1]. An advanced system for hydrogen production has been developed using electrolyte solutions that incorporate sulfur compounds. Sulfur, produced as a by-product of petroleum refining, imposes serious problems in relation to its waste disposal. The advanced hydrogen generation system using sulfur electrolyte solutions has two advantages; first it has a high efficiency rate of hydrogen utilization and recycling of waste sulfur. In the advanced hydrogen generation process, the starting solution contains S^{2-}, for effective reaction of the photocatalysis, with S_2^{2-} reacted as waste ions after

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production of hydrogen. Basic chemical reaction is as follows:

$$2HS^- \rightarrow H_2 + S_2^{2-} \tag{1}$$

As described above, engineered process for hydrogen generation from hydrogen sulfide ions in aqueous solution using solar energy with photocatalysis has been established. However sulfide ions are remained in the reacted solution after hydrogen generation. Figure 1 shows a conceptual model of sulfur cycle for hydrogen production using photochemical reaction and hydrothermal reaction. In order to design a complete closed loop of hydrogen production system, reacted sulfide ions have need to be converted into photocatalysis-active hydrogen sulfide ions. Besides, the sulfur cycle can be sustainable and environmentally friendly hydrogen supply system, by using low environmental burden heat source such as geothermal and exhaust heat from factories and generating station etc., for the hydrothermal reaction. Taking geothermal energy as an example, georeactor can be applicable to the hydrogen generator couples with solar energy. The concept of georeactor, was proposed by Takahashi et al. [2], with a plant system for utilizing subsurface geothermal energy and use of geothermal drill holes for material processing. Figure 2 shows some conceptual models of georeactor. The georeactor is characterized by direct use of geothermal energy so that the cost of energy for chemical reaction and material processing is expected to be low due to its great efficiency for heat supply.

We had focused on the self-oxidation and reduction reaction of sulfur and had studied some factors which increase a conversion rate of the reaction for the hydrogen production system, and showed that a possibility of utilization of the georeactor [3, 4]. In addition, we examined a reaction system using seawater as a practical design for the process to reduce sulfur [5, 6]. The self-oxidation and reduction reaction of sulfur cannot be discussed simply with chemical equilibria because it is a reaction with complicated sulfur compounds and processes. Here, the conversion rate is defined as ratio of reduced sulfur to elemental sulfur under some experimental reaction systems and conditions. We succeeded to reach the conversion rate of 40% as results of our experiments. Furthermore, addition of some reducers was needed to increase the conversion rate and we selected some organic materials and examined their possibilities as a reducer [7]. We already found out that organic materials had ability to reduce sulfur and the ability came out in the process of hydrothermal reaction of sulfur. In this study, we examined the effect of addition of organic matters, especially alcohols, in terms of the conversion rate.

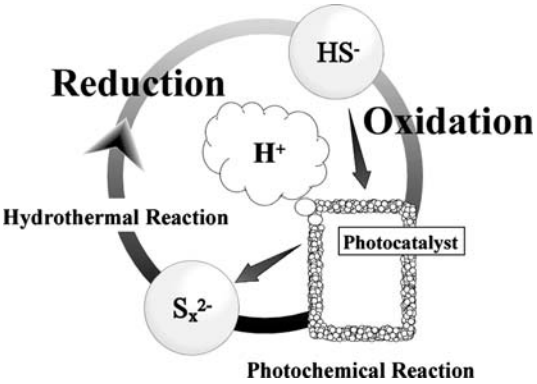

Fig. 1 Sulfur cycle in earth conscious hydrogen generation process, using solar and geothermal energies

Sulfur–water interaction

Oana and Ishikawa [8] reported the sulfur hydrolysis around 200 °C, that is hydrogen sulfide and sulfuric acid were produced. This reaction is called self-oxidation and reduction reaction (shortly self-redox reaction). In self-redox reaction, reactant is reduced and oxidized by itself simultaneously. In case of sulfur–water interaction, elemental sulfur is reduced to hydrogen sulfide (H_2S), which dissociates to HS^- and S^{2-} in alkaline solution, and elemental sulfur is also oxidized to sulfuric acid. This chemical reaction is described as follows.

$$4S_{(l)} + 4H_2O_{(l)} \rightarrow 3H_2S_{(aq)} + H^+ + HSO_4^- \tag{2}$$

At neutral pH region, hydrogen sulfide and sulfuric acid are mainly formed. At higher pH region, thiosulfuric acid and other sulfur species are formed, and these products react with elemental sulfur and dissociate to hydrogen sulfide and sulfuric acid [9, 10].

Reduction products of reaction (2), H_2S or HS^- are useful for hydrogen production. We have been examined the chemical behavior of sulfur, and corresponding self-redox reactions over a wide range of chemical conditions. Tsuchiya et al. [3] and Suto et al. [4] performed the experiments at 150–250 °C, in which starting materials were elemental sulfur and aqueous solution which initial pH was in the range from 13 to neutral conditions. Figures 3 and 4 show pH and conversion rate into S^{2-} after hydrothermal reactions at 200 °C. Their experiments showed that high alkaline conditions are the most suitable initial state to inhibit production of SO_4^{2-} and maintain neutral or weak alkaline pH conditions conductive for the formation of S^{2-}. It was also shown that the true chemical behavior of sulfur and water interaction is more complicated than the ideal reaction described by a single chemical

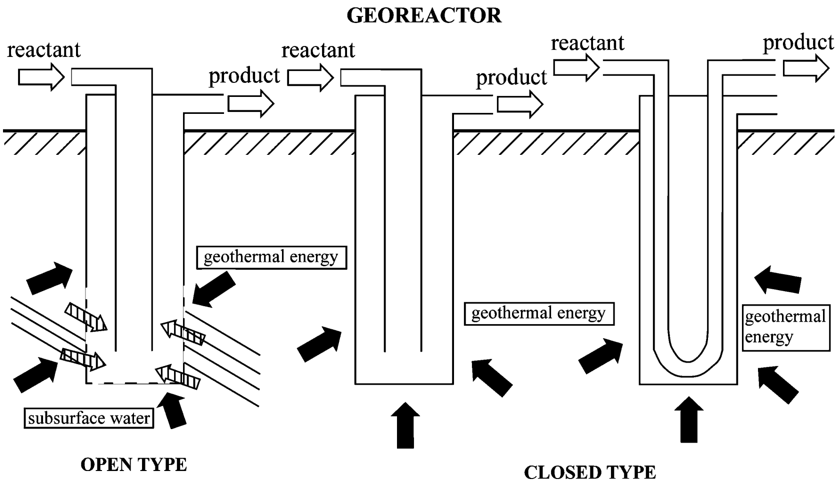

Fig. 2 Concept of georeactor

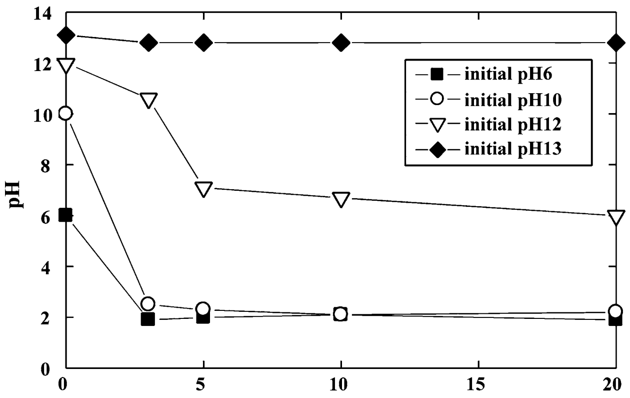

Fig. 3 Changes of pH after hydrothermal reaction with various initial pH solutions at 200 °C

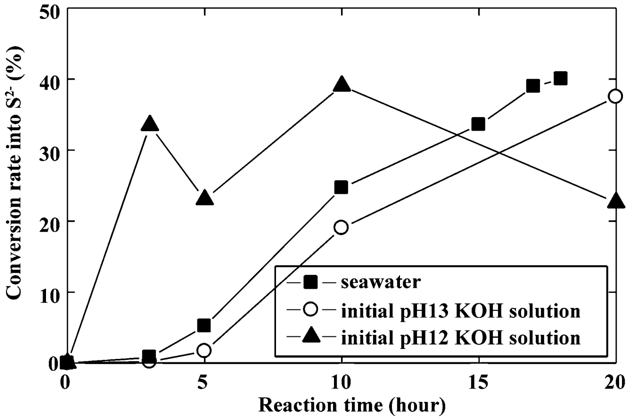

Fig. 4 Yields of S^{2-} by the hydrothermal reaction of sulfur using high pH KOH solution or seawater at 200 °C

reaction (2), because $S_2O_3^{2-}$ and SO_3^{2-} were produced at same time and these are considered as intermediate products. They reported that a conversion rate of 40% elemental sulfur into S^{2-} could be obtained after one circulation of reacted solution through the georeactor.

Those experiments indicated that more hydrogen sulfide was generated at high temperature and strong alkaline conditions. However, it is difficult to apply the reaction at strong alkaline conditions to the georeactor, because high alkaline solutions are expensive and the cost will be high to keep high alkalinity. Therefore, Tsuchiya et al. [5] and Kabuta et al. [6] suggested and reported the use of seawater (around pH 8) as a starting solution for self-redox reactions of sulfur. Seawater can be obtained cheaply and higher yields of hydrogen sulfide are expected because of its alkalinity. The conversion rate into S^{2-} (H_2S + HS^- + S^{2-}) with seawater is also given in Fig. 4. The maximum yield of S^{2-} reached about 40% by hydrothermal reaction, at 200 °C, of sulfur with seawater or strong alkaline aqueous solutions. The highest value of S^{2-} yield using seawater was nearly 50% at 3 h under 250 °C. They showed that dominant hydrogen sulfide was HS^- under weak alkaline condition of seawater, which is adequate for photocatalysis. However, S^{2-} in reacted solution decreased with reaction duration at high temperature. They considered that the decrease of S^{2-} was caused by re-reaction of S^{2-} with components in the pH-decreased seawater. Our previous works indicates that we have to reconsider the chemical reactions to describe realistic mechanisms of sulfur–water interaction at high temperatures (e.g. around 200 °C) and saturated vapor pressure, and have to find specific chemical processes which are not require sensitive control.

Sulfur–water–organic materials interaction

The self-redox reactions of sulfur are occurred inevitably during hydrogen generation in chemical cycle of sulfur. That means sulfur oxides which are useless species such as sulfuric acid and thiosulfuric acid are always formed by sulfur hydrothermal reaction. However, it is difficult to convert sulfuric acid to photocatalysis-active hydrogen sulfide by hydrothermal reaction. Therefore, alternative reducers are required to sulfur hydrothermal reaction for sustainable hydrogen generation system. In this study, organic matters are focused on as reducers of sulfur, which is ideally represented by the following formula:

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

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.

We investigated hydrothermal reaction of sulfur with many types of organic materials [7]. The results showed alcohols and formic acid shown high yields of S^{2-}. Bjerre and Sorensen [11] reported formic acid is decomposed to CO_2 and H_2 or CO and H_2O etc. CO is strong reducer but it is hardly to solve into water. Oxygen is consumed by decomposition of formic acid according to the circumstances. Due to the decomposition of formic acid, conversion rate into S^{2-} increased in hydrothermal reaction of sulfur with formic acid. On the other hand, organic matters containing benzene ring and/or compounds of big molecular weight showed low yield for reduction of sulfur.

In this study, we examined sulfur–water–organic materials (especially alcohols) interaction by batch type hydrothermal experiments to investigate optimum condition for sulfur reduction, which is great yield of reduction species without pH shift to acidic condition.

Experimental

We carried out batch type hydrothermal experiments for searching optimum condition, which is great yield of S^{2-} and low yield of SO_4^{2-}. A teflon autoclave and a hastelloy C22 autoclave were employed for hydrothermal experiment. Capacity of autoclaves was 28 mL and 40 mL, respectively. The teflon autoclave was used for experiment under atmospheric constituent condition (O_2-existed condition) and the hastelloy autoclave was used for experiment under hypoxic condition (O_2-free condition). A pressure valve for collection of gas phase was installed with a sealing corn of the hastelloy autoclave. Prior to the experiment under hypoxic condition, air in the autoclave was replaced by nitrogen gas. Pressure was adjusted at 0.2 MPa.

A high temperature dry oven with a rotation shaft for stirring was used to heat autoclaves. Reaction temperature was 200 °C, and reaction duration was 2, 4, 6, 8 and 12 h. Starting materials were elemental sulfur (5 mg) or sodium thiosulfate (18.8 mg), determined amount of alcohols and/or urea (9.4 mg). Starting solution was adjusted to 15 mL by deaerated purified water or 30% alcohol solution. Alcohols used in the experiment were methanol, ethanol, and propanol.

After reaction, pH of reacted solution was measured immediately and the solution was diluted by NaOH solution and analyzed with ion chromatography. Ion chromatography with UV spectrum and electric conductivity detector was employed to determine concentration of S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, and SO_4^{2-}. In the experiment using the hastelloy autoclave (under O_2-free condition), the quantities of CO_2 gas and H_2S gas were determined by gas chromatography.

Result and discussion

Sulfur–water–urea or alcohols interaction

Our previous studies showed weak alkaline condition of starting solution are suitable for S^{2-} generation for example the experiments of seawater. In Tsuchiya et al. [7] as mentioned above, to keep the reacted solution in weak alkaline condition and/or to increase reduction of sulfur, many kinds of organic matter was added to the reaction system. We found out that alcohols showed moderate ability for reduction of sulfur and urea could maintain weak alkaline condition. Shaw and Bordeaux [12] and Shaw and Walker [13] reported the decomposition of urea as follows:

$$(NH_2)_2CO \rightarrow NH_4^+ + NCO^- \qquad (4)$$

$$NCO^- + 2H_2O \rightarrow NH_4^+ + H_2CO_3 \qquad (5)$$

This reaction suggests alkaline condition would be obtained and maintained by hydrolysis of urea.

Changes of conversion rate of elemental sulfur into sulfur compounds by the hydrothermal reaction of sulfur and urea or ethanol (720 mg) under atmospheric constituent condition at 200 °C, are shown in Fig. 5. Sulfur hydrothermal reaction with urea shows high conversion rate of elemental sulfur (conversion rate into S^{2-} + $S_2O_3^{2-}$ + $S_2O_3^{2-}$). However, yield of S^{2-} in sulfur–water–urea system was lower than that of sulfur–water system. On the other hand, yield of $S_2O_3^{2-}$ was very significant and the highest value was 50%. With urea, pH of reacted solution was about 8. It indicates weak alkaline condition of the reacted solution was maintained by hydrolysis of urea described with reactions (4) and (5). With considering that yield of S^{2-} with urea was slightly lower than that with seawater (Fig. 4), urea can be a suitable pH controller instead of seawater. At pH 8, following self-redox reaction of sulfur occurs in addition to reaction (3):

$$4S_{(l)} + 3H_2O_{(l)} \rightarrow 2H_2S_{(aq)} + H^+ + HS_2O_3^- \qquad (6)$$

Reaction (6) means oxidation of sulfur is suspended at $S_2O_3^{2-}$ (oxidation number is 3.5). Low yield of S^{2-} with urea is appeared because conversion rate of elemental sulfur into S^{2-} by reaction (6) is lower than conversion rate of elemental sulfur into S^{2-} by reaction (3). If reduction level of the system could be increased, it is expected that formed $S_2O_3^{2-}$ is reduced and yield of S^{2-} increases.

In hydrothermal reaction of sulfur, water, and ethanol, yield of S^{2-} was higher and yield of SO_4^{2-} was lower than those in only sulfur and water system (Fig. 5). However, pH of reacted solution was decreased rapidly during reaction. Based on the increased yield of S^{2-}, it was confirmed that sulfur reduction was promoted by ethanol.

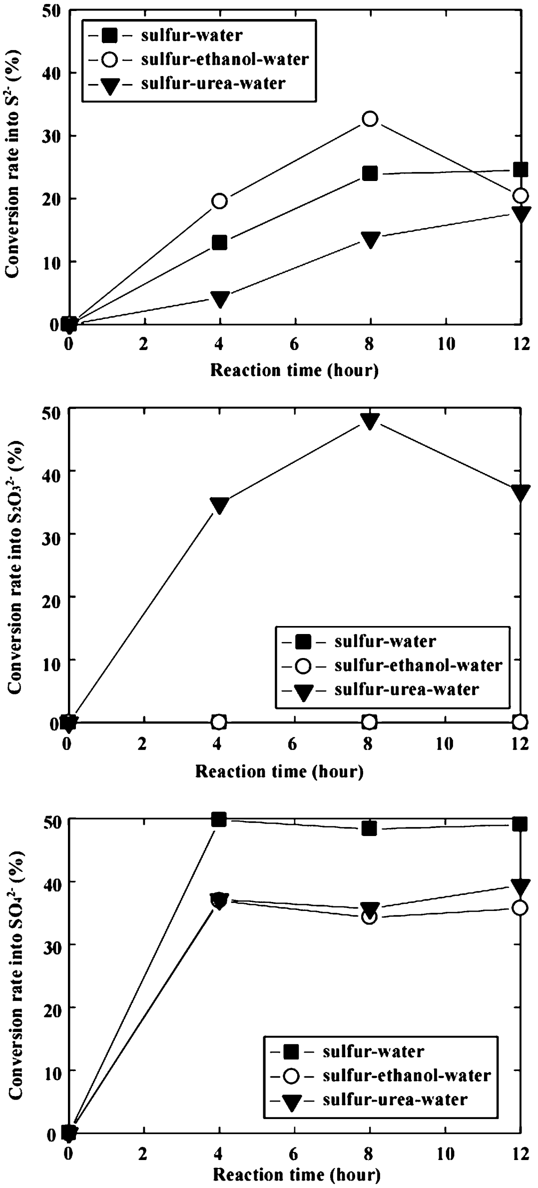

Fig. 5 Conversion rate of elemental sulfur into sulfur compounds by the hydrothermal reaction of sulfur using ethanol or urea for starting organic material

Figure 6 shows changes of conversion rate of elemental sulfur into sulfur compounds formed by hydrothermal reaction of sulfur with various amount of methanol under atmospheric constituent condition. Conversion rate of elemental sulfur into S^{2-} was increased with concentration of methanol in solution was higher, whilst conversion rate of elemental sulfur into SO_4^{2-} was suppressed.

Sulfur–water–urea–alcohol interaction

As shown in Fig. 5, by addition of urea to sulfur–water system, pH of reacted solution was maintained in weak alkaline region but reduction of sulfur was not promoted. On the other hand, by addition of alcohols to sulfur–water system, reduction of sulfur was promoted but SO_4^{2-} was formed in high value (Figs. 5 and 6) due to pH shift to acidic region. Therefore, to increase formation of S^{2-} much more, addition of both urea and alcohols was considered as a useful method. Change of conversion rate of elemental sulfur into sulfur compounds by hydrothermal reaction of sulfur with urea and alcohols under atmospheric constituent condition at 200 °C are shown in Fig. 7.

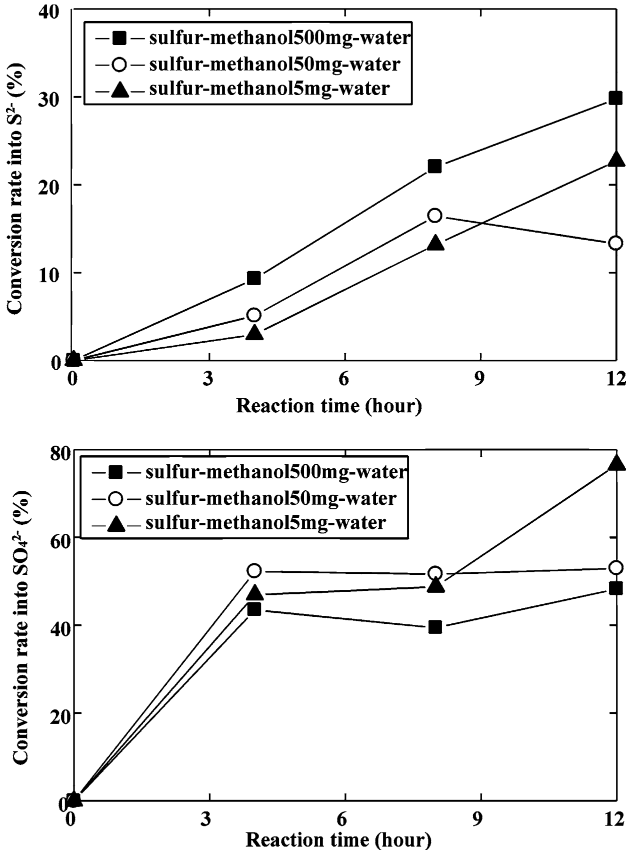

Fig. 6 Conversion rate into sulfur compounds by the hydrothermal reaction of sulfur with various concentration of methanol solution at 200 °C

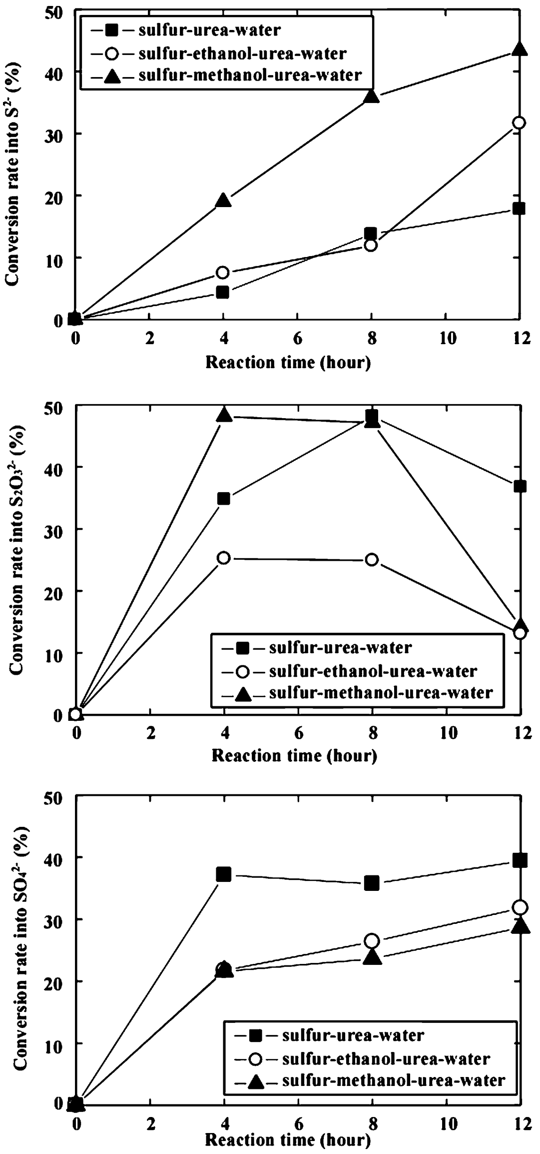

Fig. 7 Conversion rate into sulfur compounds by the hydrothermal reaction of sulfur with urea and alcohols under atmospheric constituent condition at 200 °C. Thirty percent alcohol solution was used

Ethanol (720 mg) and methanol (500 mg) were used. As shown in Fig. 7, addition of urea and ethanol increased yield of S^{2-} to 2.5 times greater than that with addition of only urea and decreased yield of $S_2O_3^{2-}$ and SO_4^{2-} compared with addition of only urea and addition of only ethanol (Fig. 5). Addition of urea and methanol increased yield of S^{2-} after 12-h reaction compared with addition of only urea and decreased yield of SO_4^{2-} as same as case of ethanol. Yields of S^{2-} by the hydrothermal reaction of sulfur–ethanol–urea and sulfur–methanol–urea were over 40% and about 35% respectively. It suggests that urea promotes efficiency of reduction by alcohols, which reduce sulfur to S^{2-}. Yield of $S_2O_3^{2-}$ by hydrothermal reaction of sulfur–urea–methanol was two times greater than that by hydrothermal reaction of sulfur–urea–ethanol after 4 and 8-h reactions, but both decreased to 15% after 12 h. If the formation of $S_2O_3^{2-}$ was occurred only by urea, decomposition or reduction of $S_2O_3^{2-}$ to S^{2-} and SO_4^{2-} by hydrothermal reaction of sulfur–urea–ethanol is faster than that by sulfur–urea–methanol.

Figures 5–7 show that synergy effect were obtained by addition of both urea and alcohol. To estimate effect of additions without oxygen, some experiments under O_2-free condition were conducted. Figure 8 provides the result of hydrothermal reactions of sulfur–urea–alcohol under hypoxic condition at 200 °C. Starting materials were sulfur, urea and 30% alcohol aqueous solution. Methanol, ethanol, and propanol were used. Changes of conversion rate of elemental sulfur into sulfur compounds shown in Fig. 8, inferred that reaction reached static state after 6 h. Yield of S^{2-} was drastically increased and yield of SO_4^{2} was significantly suppressed below 10% by removing O_2 from the system for both case of methanol and ethanol, compared with under atmospheric constituent condition (Fig. 7). As shown in Fig. 8, conversion rate into S^{2-} reached to 80% with methanol and 60% with ethanol. Complete conversion (100% yield of S^{2-}) was achieved by using urea and propanol. Even though the molecular weight is methanol < ethanol < propanol, the yields of S^{2-} were ethanol < methanol < propanol. At the experiments under atmospheric constituent condition, S^{2-} yields from hydrothermal reaction of sulfur–urea–ethanol was higher than that from sulfur–urea–methanol (Fig. 7), which was opposite to under hypoxic condition (Fig. 8). Therefore low yield of S^{2-} by the reaction of sulfur–urea–ethanol under hypoxic condition may be caused by materials of inner wall (teflon or hastelloy C22) or gas phase components. A slight amount of gray precipitation was observed on inner wall of autoclaves after the experiments of sulfur–urea–ethanol. It is considered as elemental sulfur or formed S^{2-} reacted with the inner wall.

As shown in Fig. 8, although yields of S^{2-} and SO_4^{2-} from hydrothermal reaction of sulfur–urea–alcohol increased with reaction duration, yield of $S_2O_3^{2-}$ was highest after 2 h and decreased rapidly. During the decreasing of $S_2O_3^{2-}$ yield, conversion rate of elemental sulfur into S^{2-} increased and yield of SO_4^{2-} was nearly constant. Hence, it can be considered that in sulfur hydrothermal reaction with urea and alcohol, early-formed $S_2O_3^{2-}$ was mainly reduced to S^{2-}. These facts indicate a possibility that $S_2O_3^{2-}$ is reduced to S^{2-} by alcohol. Small amount of formic acid was detected in the experiments using methanol or ethanol and large amount of CO_2 was detected in all experiments with sulfur–urea–alcohols. This indicates that alcohols were oxidized to formic acid or CO_2 in compensation for sulfur reduction.

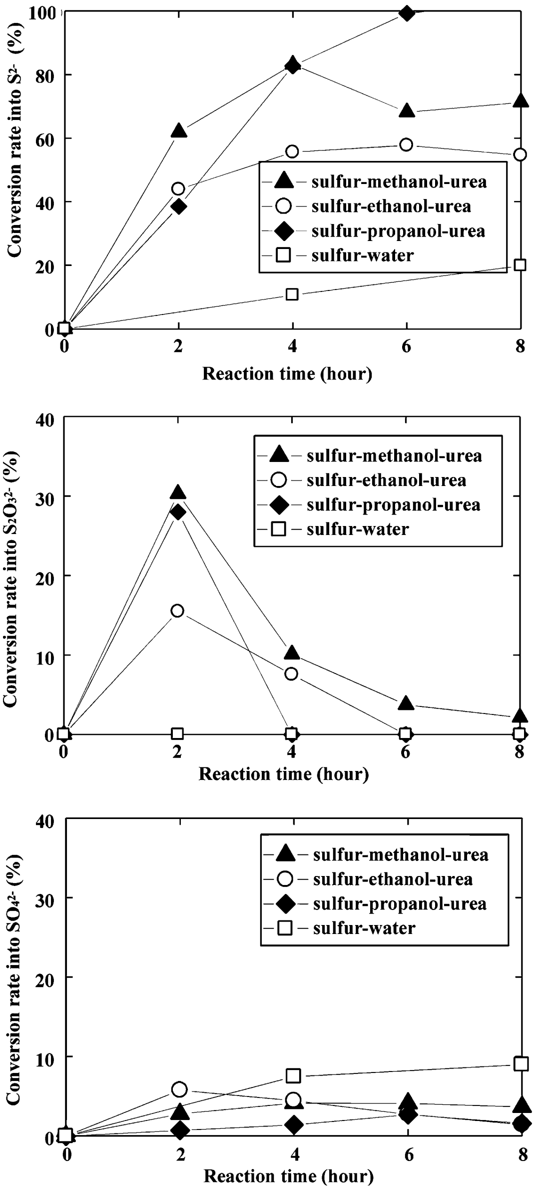

Fig. 8 Conversion rate into sulfur compounds by the hydrothermal reaction of sulfur with urea and alcohols under hypoxic condition at 200 °C. Thirty percent alcohol solution was used

In order to investigate the mechanism of decreasing the formed $S_2O_3^{2-}$, the hydrothermal experiments using $S_2O_3^{2-}$ as a starting material were carried out. Three sets of starting materials were prepared. First was only sodium thiosulfate and purified water for $S_2O_3^{2-}$ hydrothermal reaction. Second was sodium thiosulfate with urea and purified water for $S_2O_3^{2-}$ hydrothermal reaction in alkaline condition. Third was sodium thiosulfate with urea and 30% propanol solution for $S_2O_3^{2-}$ reduction by propanol in alkaline condition. Figure 9 shows conversion rate of $S_2O_3^{2-}$ into another sulfur compounds by the experiments under hypoxic condition.

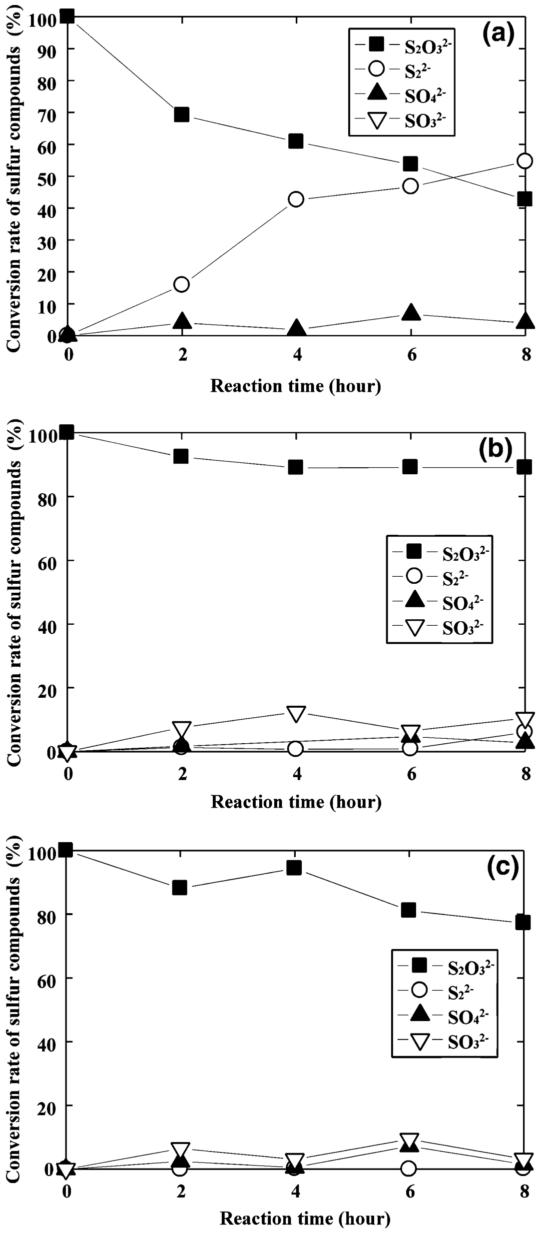

Fig. 9 Changes of yields of thiosulfate into sulfur compounds by hydrothermal reaction of sodium thiosulfate under hypoxic condition at 200 °C (**a**) sodium thiosulfate, urea, and 30% propanol solution (**b**) sodium thiosulfate and urea and water (**c**) sodium thiosulfate and water

In the sodium thiosulfate-water system (Fig. 9c) and the sodium thiosulfate–water–urea system (Fig. 9b), decreasing of $S_2O_3^{2-}$ which is corresponding to conversion of $S_2O_3^{2-}$ into sulfur compounds was very slight, and it was resulted in a small amount of formation of S^{2-} and sulfuric acids (lower than 10%). Contrastively in the sodium thiosulfate–water–urea–propanol system (Fig. 9a), decrease of $S_2O_3^{2-}$ was progressed with reaction duration and 60% of thiosulfate ion was decomposed to S^{2-} and SO_4^{2-} after 8 h. Yield of S^{2-} was large with suppression of yield of SO_4^{2-}, and it is clear that $S_2O_3^{2-}$ was mostly reduced to S^{2-}. These results confirmed that reduction of $S_2O_3^{2-}$ without alcohols is blocked by urea as shown in Fig. 5 and alcohol as reducer is an essential component. Based on these experimental results, following reaction schemes could be considered in the hydrothermal reaction of sulfur with urea and propanol shown in Fig. 8.

$$9S + C_3H_7COH + 5H_2O \rightarrow 9S^{2-} + 3CO_2 + 18H^+ \tag{7}$$

$$9S + C_3H_7COH + 5OH^- \rightarrow 9S^{2-} + 3CO_2 + 18H_2O \tag{8}$$

Conclusions

In this study, we focused on the sulfur–water–organic materials interaction. Particularly, conversion of waste elemental sulfur into useful hydrogen sulfide ion for the hydrogen production system with photocatalysis using solar energy, was considered. The experiments of hydrothermal reaction of sulfur with organic materials were performed with the purpose of generating more hydrogen sulfide and inhibiting SO_4^{2-} generation. The conclusions are follows:

(1) It is important to keep solution in weak alkaline region and urea is useful and efficient as a pH controller.

(2) Alcohols, particularly propanol, have a great effect on reduction of elemental sulfur and thiosulfate ion to hydrogen sulfide ion, and are required to achieve high conversion rate into hydrogen sulfide ion with inhibiting oxidation to sulfate.

References

1. Arai T, Sakima S, Yoshimura H, Shinoda K, Jeyadevan B, Tohji K, Kasuya A, Hishina Y (2001) In: Proceedings of International Symposium On Cluster Assembled Materials IPAP Conference Series 3, 2001, p 75
2. Takahashi H, Shoji T, Nakatsuka K, Abe H (1987) Geothermal Energy Symposium ASME/GRC, p 33
3. Tsuchiya N, Suto Y, Nakatsuka K (2003) Geotherm Res Coun Trans 27:111
4. Suto Y, Takano Y, Kabuta T, Tsuchiya N, Nakatsuka K (2003) In: Proceedings of 7th International Symposium of Hydrothermal Reaction, p 523
5. Tsuchiya N, Tohji K, Bignall G (2004) In: Proceedings of New Zealand 26th Annual Geothermal Workshop, TAUPO, December, CD-ROM
6. Kabuta T, Suto Y, Tsuchiya N (2005) Geotherm Res Coun Trans 29:747
7. Tsuchiya N, Suto Y, Morikawa S, Kabuta T, Yokoyama S (2006) In: Proceedings of the Renewable Energy 2006, Chiba, Japan, October, 2006 (in press)
8. Oana S, Ishikawa H (1966) Geochem J 1:45
9. Ellis AJ, Giggenbach W (1971) Geochim Cosmochim Acta 35:247
10. Giggenbach W (1974) Inorg Chem 13(7):1724
11. Bjerre AB, Sørensen E (1992) Ind Eng Chem Res 31:1574
12. Shaw WHR, Bordeaux JJ (1955) J Am Chem Soc 77:4729
13. Shaw WHR, Walker GD (1958) J Am Chem Soc 80:5337