

Correlation of H₂S and COS in the hot coal gas stream and its importance for high temperature desulfurization

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Abstract—Thermodynamic analysis of the correlation of H₂S and COS has been carried out at the temperature range of 400–650 °C at which high temperature desulfurization of coal gas is usually performed. The correlation of the two sulfur species is mainly through the reaction $\text{H}_2\text{S} + \text{CO} \rightarrow \text{COS} + \text{H}_2$. Simulated coal gas with the following composition CO 32.69%, H₂ 39.58%, CO₂ 18.27%, N₂ 8.92% and H₂S 0.47% was used in this study, and the equilibrium concentrations of the two species at different temperatures were calculated. The results of Fe-based sorbents during sulfidation were compared with calculations. It is concluded that the above reaction may reach equilibrium concentration in the presence of the Fe-based sorbents, which means the Fe-based sorbents may effectively catalyze the reaction between H₂S and CO. Because of the correlation of the two sulfur species, both can be effectively removed at high temperatures simultaneously, offering high temperature desulfurization some advantages over low temperature desulfurization processes.

Key words: Hot Coal Gas Cleaning, Desulfurization, COS Formation, Coal-gasification-based Poly-generation

INTRODUCTION

China heavily relies on coal to supply its primary energy now and in the future. Gasification-based clean coal technology such as the poly-generation system is seen as one of the major options to secure the energy supply for China in compliance with tougher environmental regulations in the future. Removal of sulfur species at high temperatures is a crucial part of the development of poly-generation systems [1]. Under gasification conditions, the sulfur species contained in the hot coal gas stream are complicated, but mainly H₂S, COS and CS₂. The concentration of the rest is negligible. Thermodynamically, the concentration of H₂S and COS is strongly correlated [2] through reaction (1) and may be affected by the conditions of the system such as temperature and the presence of catalysts.



The properties of COS have been reviewed by Ferm [3] and more recently updated by Svoronos et al. [4]. In the gasification coal gas stream, the COS content was usually found to be 10–15% of the H₂S content and formation of COS from H₂S is certainly taking place [5]. In the literature [2,6–9], it has been generally agreed that reaction (1) is responsible for the formation of COS in the hot coal gas stream from H₂S while the following reaction plays little role.



Removal of COS is as important as the removal of H₂S and is de-

sirable for IGCC or poly-generation systems. At low temperatures, the removal of COS is through hydrolysis reaction of COS, i.e., the reverse reaction of reaction (2) [10–12] followed by adsorption of H₂S using sorbents. The hydrolysis reaction is expressed as:



During desulfurization experiments [1,13,14], COS is detected in the hot coal gas stream at the later stage of sulfidation with substantially high conversion of H₂S, and the concentration of the two species is strongly correlated in the presence of sorbents [1,13]. In the poly-generation system, desulfurization is performed in the temperature range 400–650 °C. If this correlation is rectified in this temperature range and if COS in the hot coal gas stream can be converted to H₂S, it is then possible that both sulfur species can be removed by Fe-based sorbents, which is preferably used for desulfurization systems. In this paper, we discuss the thermodynamic correlation between H₂S and COS in a great detail and offer some experimental results.

1. Thermodynamic Analysis

The reactions (1) and (2) have been discussed in the literature [2–5,7–9,12,14–16] and catalyzed reaction (1) has also been studied [3,17]. Other possible reactions discussed in the literature [3,8] involving the two sulfur species in the hot coal gas streams at different temperatures include:



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Reactions (4) to (9) usually take place at temperatures above 1,000 °C. Reaction (10) may take place at low temperatures in the presence of MoS₂ catalyst [18]. In the present study, neither elemental sulfur nor CS₂ has been observed, indicating that those reactions did not take place under the conditions in the present study. Therefore, the most important reaction that determines the concentration of COS and H₂S in the hot coal gas stream is reaction (1).

Some thermodynamic data are available in the literature [2,6-8, 16]. The data cover a temperature range from room temperature to 1,200 °C. The reaction is slightly exothermic with the reaction heat of -2.58 kcal/mol and equilibrium constant of 0.53 at room temperature [2]. Hot coal gas desulfurization is usually carried out at temperatures between 350 °C and 700 °C, while the Claus furnace is usually operated above 950 °C. The relationship of free energy ΔG and equilibrium constant K_{eq} versus temperature is illustrated in Fig. 1. It can be seen that ΔG of the reaction has a linear relationship with temperature while K_{eq} decreases exponentially when the temperature increases. Therefore, the equilibrium concentration of COS in a gas stream decreases correspondingly with increasing the temperature.

At temperatures where hot coal gas desulfurization is performed, a water-gas-shift reaction may occur in the hot coal gas stream in the presence of catalyst [19,20]:



Reaction (11) will change the concentrations of the major gas components (i.e., CO, H₂, CO₂ and H₂O) which may further influence the conversion of H₂S to COS through reaction (1). By considering both reaction (1) and (11), the equilibrium concentration of COS in the hot coal gas stream has been calculated based on the simulated coal gas composition used in this study for hot coal gas desulfurization experiments, and the results are shown in Fig. 2.

It can be seen that below 550 °C the equilibrium COS partial pressure decreases exponentially when the temperature increases, which is determined by the equilibrium constants of reactions (1) and (11). However, a further increase in the temperature leads to a slight in-

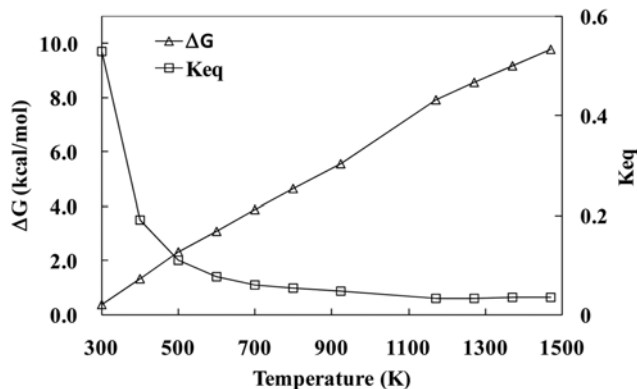


Fig. 1. Some thermodynamic data of reaction (1) from literature [2,6-8].

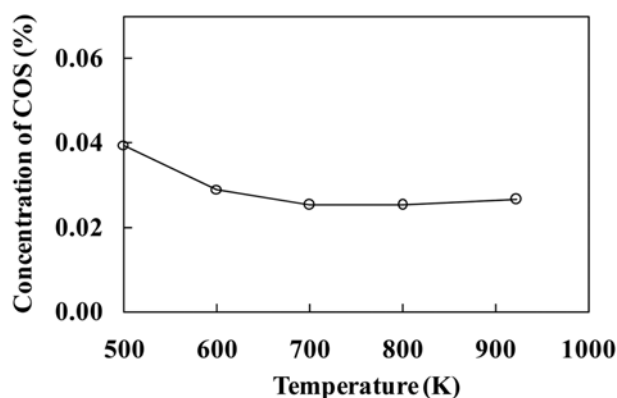


Fig. 2. Thermodynamic concentration of COS in the hot coal gas stream with the following initial composition CO 32.69%; H₂ 39.58%; CO₂ 18.27%; N₂ 8.92%; H₂S 0.47%.

crease in the COS partial pressure. In the presence of catalysts or if the reaction time is long enough allowing for equilibrium, the conversion of H₂S to COS will follow the above curve. However, under the present experimental conditions, at temperatures below 900 °C, the reaction will be limited by the kinetic rates in the absence of catalyst, as will be discussed below. In this case, the COS partial pressure will increase with increasing the temperature, as reported in the literature [9]. In practice, the gas residence time in the gas cleaning units generally allows for the equilibration of the reaction. Therefore, the thermodynamic calculation results are instructive for practical situations of hot coal gas desulfurization.

2. Experimental Results

2-1. COS Formation in the Absence of Catalyst

Experiments were carried out [13,21] at 400-600 °C using the simulated coal gas with the composition indicated in Fig. 2, and the experimental setup has been described elsewhere [1]. The coal gas stream passed through a quartz reactor heated using an electric furnace. No catalyst was loaded into the reactor and the space velocity was 1,000 h⁻¹. The outlet gas was analyzed using a GC equipped with FPD and TCD.

Different from the thermodynamic calculation, the concentration of COS converted from H₂S increased when the temperature in-

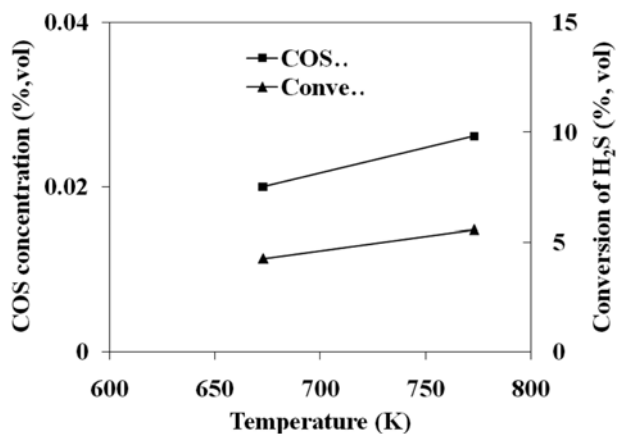


Fig. 3. Experimental data on conversion of H₂S to COS in simulated coal gas.

creased from 400 °C to 600 °C, and correspondingly the conversion of H₂S increased as well, as shown in Fig. 3. This is because the reaction rate is limited at low temperatures and cannot reach equilibrium with the current reactor configuration. But the reaction rate increases with increasing the temperature. Therefore, the conversion of H₂S to COS increased with increasing the temperature. This result is consistent with other research [9]. According to the literature [9], the direct reaction between CO and H₂S may be described by the rate expression:

$$r_{\text{cos}} = k_3 C_{\text{co}} C_{\text{H}_2\text{S}}^{0.5} \quad (12)$$

where the rate constant was expressed as:

$$k_3 = 1.59 \pm 0.86 \times 10^5 \exp[(-13340 \pm 930 \text{ K})/T] (\text{m}^3/\text{kmol})^{0.5}/\text{s} \quad (13)$$

One possible mechanism involved in the reaction between CO and H₂S could be the production of the SH radical via decomposition of H₂S and subsequent reaction between CO and the SH radical to produce COS and the H radical. The concentration of SH radical was proportional to the square root of H₂S concentration in the gas stream.

Experiments were also performed with the COS+H₂ reaction system in the absence of catalyst in the temperature range of 400 °C to 600 °C, and the transformation of COS to H₂S was not evident. The result confirms that the reverse reaction (1) will not occur without

catalyst. We also confirmed that reaction (2), i.e., the reaction of H₂S with CO₂, at the temperature of interest is negligible without catalysts.

2-2. Conversion of H₂S to COS in the Presence of Fe-based Sorbents

The formation of COS in the hot coal gas stream was studied by Oakey et al. [5]. It has also been reported in our previous experiments [1,13]. The simulated coal gas with the composition indicated in Fig. 2 passed through the quartz reactor loaded with Fe-based sorbents. The experimental setup is described elsewhere [1, 13]. The inlet gas stream did not contain COS. Both Fe-Ce and Fe-Mo sorbents supported on fine coal ash were used. The sorbents were prepared with physical mixing method and the sorbent particles were cylindrical with a size of $\phi 2 \times 2$ mm. The sorbent samples were dried at 110 °C and calcined at 750 °C for 4 hours before use. The reactor was heated by an electric furnace in the temperature range 400–600 °C. Concentration of COS and H₂S was measured by using the GC with FPD detector.

Sulfidation curves of Fe-Ce sorbents at different temperatures with the Fe : Ce mole ratio of 4 : 1 in the sorbents are shown in Fig. 4. The sorbent Fe : Ce mole ratio of 4 : 1 was chosen according to experiments with which the sulfidation performance of the sorbent was optimal. The ratio of (Fe/Ce) : (ash supporter) : binder was 8 : 2 : 1. It can be seen that the changes in the concentration of H₂S

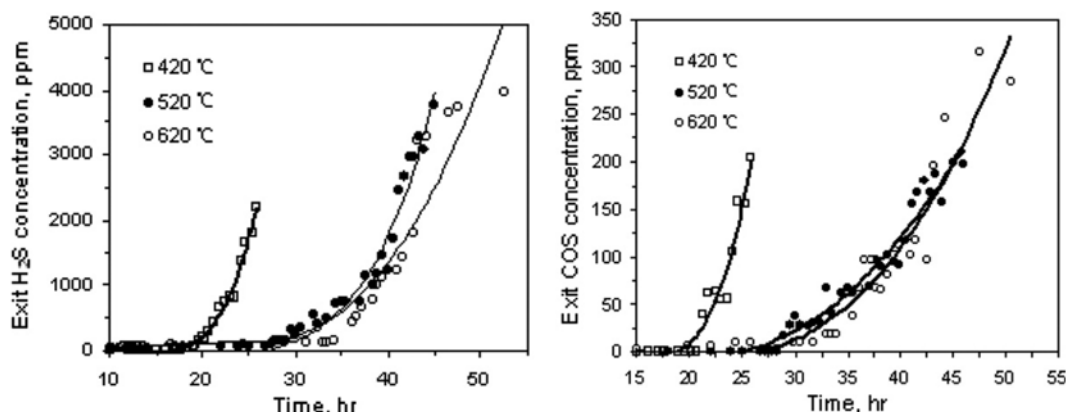


Fig. 4. Sulfidation curves of supported Fe-Ce sorbent at different temperatures (ratio of Fe : Ce is 4 : 1, ratio of (Fe/Ce) : ash : binder = 8 : 2 : 1) [1,21].

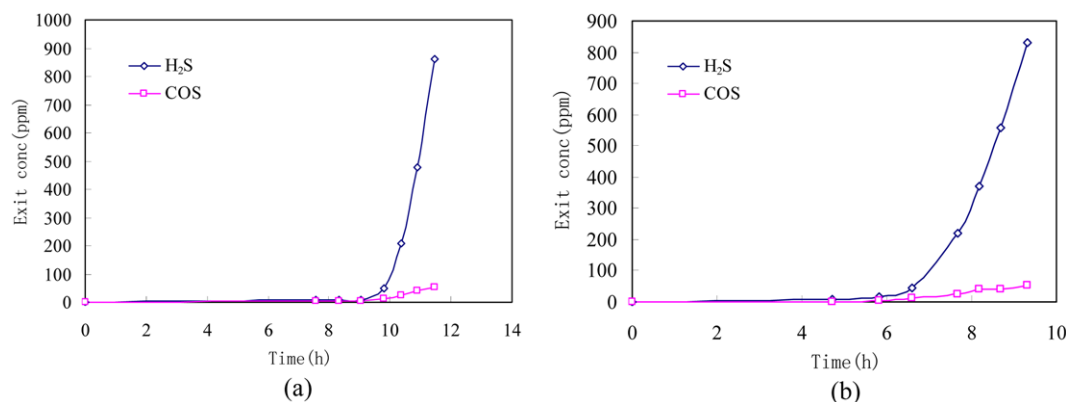


Fig. 5. Sulfidation curves of supported Fe-Mo sorbents at 500 °C with ratio of (Fe/Mo) : ash : binder at 4 : 5 : 2 [13]. (a) ratio of Fe : Mo is 6 : 1; (b) ratio of Fe : Mo is 4 : 1.

and COS are strongly correlated at all temperatures. During early sulfidation stage, H₂S concentration in the exit gas stream was very low, less than 100 ppm, while COS concentration was hardly detectable. As the sulfidation reaction proceeded, once the sorbents were sulfidated, the concentration of H₂S increased quickly. Correspondingly, the concentration of COS also increased. At all temperatures, the COS curves had a similar shape to that of H₂S curves.

Similar results were obtained from sulfidation experiments using Fe-Mo sorbent at 500 °C, as is shown in Fig. 5. Different Fe : Mo mole ratios, i.e., 6 : 1 and 4 : 1, were used. The ratio of (Fe/Mo) : (ash supporter) : binder was 4 : 5 : 2. The trend of H₂S and COS concentration during sulfidation of both Fe-Mo sorbents was similar to the Fe-Ce sorbent case. It is likely that sulfidated metal oxides, i.e., the metal sulfides, may have acted as the catalysts for reaction (1).

2-3. Possible Routine of COS Removal from Hot Coal Gas

The correlation between COS and H₂S may play a critical role during hot coal gas desulfurization, in particular for the removal of COS. The removal of COS may be in three possible routines, through the hydrogenation of COS (the reverse reaction of reaction (1)); through hydrolysis of COS (reaction (3)); or through direct reaction of COS with metal oxides. Direct reaction of metal oxide with COS to form metal sulfide and carbon dioxide has been given in the literature [5] and is expressed as:



The first two routines will convert COS to H₂S followed by the reaction of H₂S with metal oxides to form metal sulfides. However, at high temperatures, the hydrolysis reaction will not be important in determining COS concentration because COS and H₂S concentration will be eventually determined by reaction (1), which is catalyzed by transition metal oxides or sulfides, no matter what routine it takes for desulfurization. Through these mechanisms, the simultaneous removal of COS and H₂S may be easily realized by using cheap Fe-based sorbents, offering high temperature desulfurization some advantages over low temperature desulfurization processes.

CONCLUSIONS

Strong correlation exists between hydrogen sulfide and carbonyl sulfide at hot coal gas desulfurization temperatures through the reaction $\text{H}_2\text{S} + \text{CO} \rightarrow \text{COS} + \text{H}_2$. At low temperatures, the reaction is controlled by its kinetic rate. In the presence of the Fe-based sorbents, the reaction may reach equilibrium concentration. This means the Fe-based sorbents may effectively catalyze the reaction between H₂S and CO. Therefore, by using Fe-based sorbents, both sulfur species can be removed simultaneously from hot coal gases.

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