Korean J. Chem. Eng., **18**(5), 635-639 (2001)

Desulfurization Characteristics of CuO-Fe_2O_3 Sorbents

Hyo-Song Lee, Min-Pil Kang, Yun-Seob Song, Tae-Jin Lee* and Young-Woo Rhee†

*School of Chemical Engineering and Technology, Yeungnam University, Gyongsan 712-749, Korea
Department of Chemical Engineering, Chungnam National University, Daejeon 305-764, Korea

(*Received 19 March 2001 • accepted 26 May 2001*)

Abstract—A series of CuO-Fe_2O_3 sorbents with 25 wt% SiO_2 as a support were prepared based on a simple mixing method in order to evaluate the effects of Fe_2O_3 on their desulfurization reactivities. The initial reactivities of sorbents were tested by using a TGA and their cyclic performance was investigated in a GC/microreactor system. The activation energy calculated by the Chatterjee-Conrad method based on the TGA experiment decreased as the content of Fe_2O_3 increased. Sulfur loading in the cyclic reactions increased with increase of Fe_2O_3 content, and its maximum value was 8.9 g sulfur per 100 g sorbent.

Key words: CuO-Fe_2O_3 Sorbent, Desulfurization, Regeneration Cyclic Reaction

INTRODUCTION

The IGCC (Integrated coal Gasification Combined Cycle) technology has been widely studied as a promising new candidate for coal utilization technology due to its high heat efficiency. However, the desulfurization unit must be applied in order to remove H_2S out of coal gas evolved from the gasifier. Since H_2S contained in coal gas is very corrosive to metallic equipment, the coal gas should be purified prior to entering the gas turbine [Ryu et al., 1998; Choi et al., 1994; Moon et al., 1994; Kang et al., 1997; Lee et al., 1991; Park et al., 1998; Jeon et al., 1995, 1997].

Westmoreland and Harrison have performed extensive thermodynamic screening tests of desulfurization potential at high temperatures for 28 basic metal oxides. They investigated the equilibrium sulfur removal and stability of solid mixtures up to 1,500 °C based on the free energy minimization technique. Based on the experimental results they suggested that 11 elements, i.e., Fe, Zn, Mo, Mn, V, Ca, Sr, Ba, Co, Cu and W, have the thermodynamic feasibility [Westmoreland and Harrison, 1976]. Ayala et al. investigated the thermodynamic equilibrium concentration of H_2S for several metal oxides in the range of 350-550 °C. Metals tested in their study were Cu, Zn, Fe, Ni, Sr, Co, Mo, Mn, CuO and W. CuO showed the lowest H_2S equilibrium concentration, whereas copper metal showed the highest. This implies that CuO could be a very promising candidate for desulfurization sorbent if reduction of CuO to Cu is minimized [Ayala et al., 1997; Javad et al., 1997; Lee et al., 1997]. Song et al. and other researchers investigated the suitability of zeolite, γ-alumina, SiO_2 for a support of CuO-based sorbent. CuO-based sorbent supported on SiO_2 showed the best desulfurization performance. Also, in order to study the effect of SiO_2 content on structural stability in long-term cyclic reactions, a series of sorbents of which SiO_2 contents are 0, 15, 25, and 35 wt% were prepared. It was reported from this study that the sorbent of 25 wt% SiO_2 has the structural stability and maximum utilization efficiency of copper [Song et al., 2000; Yi et al., 1999; Joen et al., 1997]. Kyotani et al. investigated desulfurization abilities of several CuO sorbents including pure CuO, physical mixture of CuO and SiO_2, CuO supported on SiO_2, CuO dispersed on SiO_2, and CuO supported on zeolite. It was found that the supported CuO sorbents have high reactivities in both desulfurization and regeneration steps and show no reduction in reactivities during cyclic reactions. However, the reactivity of the physically mixed CuO sorbent showed almost the same as that of the supported sorbents [Kyotani et al., 1989].

In this study a series of CuO-Fe_2O_3 sorbents supported on 25 wt% SiO_2 were prepared in order to investigate effects of Fe_2O_3 content on the performance of CuO-Fe_2O_3 sorbents. Desulfurization and regeneration reactions were carried out at 500 °C and 700 °C, respectively. Reaction characteristics and desulfurization abilities of sorbents were investigated by TGA and cyclic reaction tests.

METHODS

1. Sorbent Preparation

25 wt% SiO_2 was used as a support and the ratios of CuO to Fe_2O_3 were 9 : 1, 8 : 2, 7 : 3. Based on SiO_2 content, sorbents were named as CFS1, CFS2 and CFS3. The composition of sorbents is summarized in Table 1. Simple mixing was applied in preparing sorbents instead of more sophisticated sorbent preparation methods such as precipitation and impregnation methods due to economic feasibility. It has been reported that no significant differences existed in the performances of sorbents prepared using both the simple and sophisticated methods. [Kyotani et al., 1989]. A raw mixture of de-

Table 1. composition of CuO-Fe_2O_3 sorbents (wt%)

Sorbents	CuO	Fe_2O_3	SiO_2
CS3	75	-	25
CFS1	67.5	7.5	
CFS2	60	15	
CFS3	52.5	22.5	

---

†To whom correspondence should be addressed.
E-mail: ywrhee@cuvic.cnu.ac.kr
‡Presented at the Int'*l* Symp. on Chem. Eng. (Cheju, Feb. 8-10, 2001), dedicated to Prof. H. S. Chun on the occasion of his retirement from Korea University.

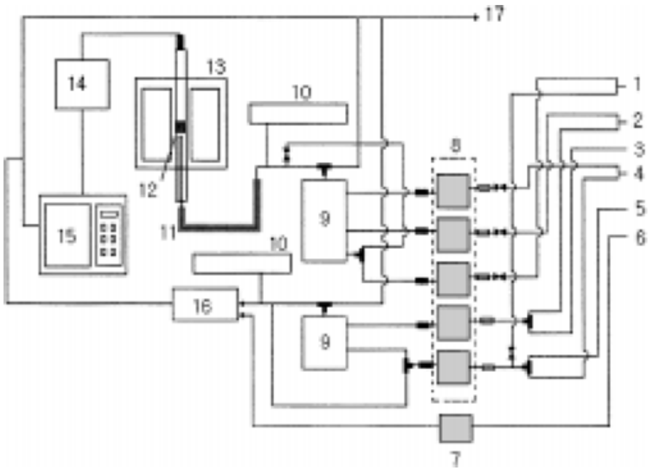

Fig. 1. Schematic diagram of experimental apparatus.

1. N_2
2. H_2S
3. SO_2
4. Mixing gas
5. Air
6. N_2
7. Flow meter
8. MFC
9. Mixing tank
10. Syringe pump
11. Heating tape
12. Sample
13. Microreactor
14. Water trap
15. GC
16. TGA
17. Vent

sired composition was well mixed in a ball mill for 6 hours and then the mixture was pasted by adding ethylene glycol. The paste was extruded by using an extruder, and the extrudates were dried in an oven at 200 °C for 4 hours. Dried extrudates were further calcined in a furnace at 700 °C for 4 hours and finally crushed and sieved to a size of 92-106 μm.

2. Experimental Procedure

The experimental apparatus consists of two main parts: TGA and GC/microreactor systems as can be seen in Fig. 1. A TGA2050 TGA and M600D GC were used. The flow rates of reaction gases are controlled by MFCs. After being well mixed in a mixing tank, the gases are introduced into either TGA or GC/microreactor system. The composition of simulated gas is summarized in Table 2. Water was injected into the gas stream by a syringe pump, and in order to make the injected liquid water the water vapor, all the gas lines were heated by using a heating tape. About 10 mg of sample was used for TGA experiments and about 3 g for GC/microreactor experiments. The microreactor was made of quartz and its diameter was 25.4 mm. A thermocouple was placed inside the reactor to monitor the reaction temperature.

Table 2. Composition of simulated gas

	Sulfidation			Regeneration	
	TGA	GC/microreactor		TGA	GC/microreactor
H_2	11.82%	11.82%	O_2	5%	5%
CO	19.18%	19.18%			
CO_2	7.0%	7.0%			
H_2S	0.28%	1%	N_2	Balance	Balance
H_2O	-	10.8%			
N_2	Balance	Balance			

The TGA experiments were performed in two modes. One was the 1.5 cycle reaction of a general reaction sequence of desulfurization-regeneration-desulfurization. The other mode was the full reduction followed by desulfurization where the maximum amount of reduction or the maximum sulfur loading of sorbent can be measured. In the latter mode the sorbent was fully reduced in a reducing gas stream containing no H_2S, and after no further weight change was observed the simulated gas was introduced for desulfurization. In GC/microreactor experiments a cyclic reaction of desulfurization and regeneration was repeated, and in order to reduce the reaction time 1% H_2S was used. The concentration of H_2S was analyzed by GC equipped with a TCD.

RESULTS AND DISCUSSION

1. TGA Experiments

In TGA experiments, reduction of $CuO-Fe_2O_3$ results in a weight gain and its desulfurization a weight loss. The maximum sulfur loading of sorbent can be calculated based on the weight gain obtained from the desulfurization after reduction. In Fig. 2 results for $CuO-Fe_2O_3$ sorbents performed at a desulfurization temperature of 500 °C and a regeneration temperature of 700 °C are compared with CS3 sorbent that contains 75 wt% CuO and 25 wt% SiO_2 [Song et al., 2000]. The amount of reduction increases with Fe_2O_3 content, showing more weight loss on the graph. Results of 1.5 cycle reactions performed at the desulfurization temperature of 500 °C and the re-

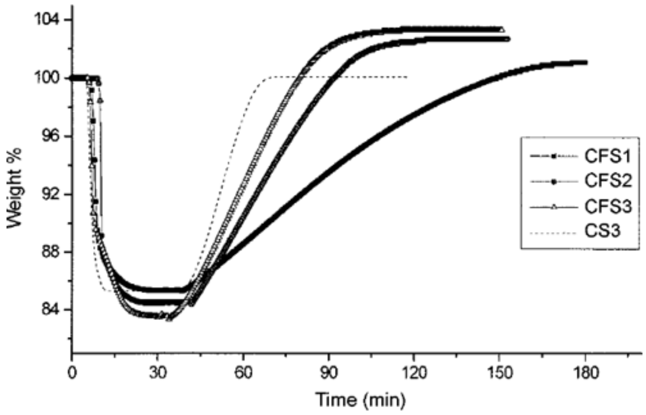

Fig. 2. TGA curves for sulfidation reactions of $CuO-Fe_2O_3$ sorbents.

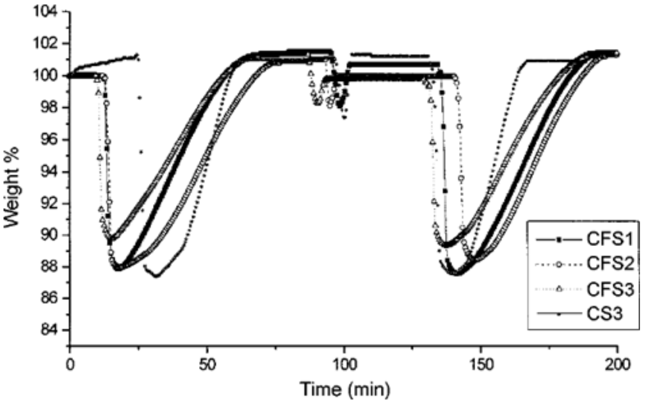

Fig. 3. TGA curves for cyclic reactions of $CuO-Fe_2O_3$ sorbents.

Table 3. Sulfur loadings of CuO-Fe_2O_3 sorbents (g sulfur/100 g sorbent)

	CS3	CFS1	CFS2	CFS3
Red. and sul. test	14.8	15.7	18.2	19.8
TGA test 1st cycle	13.6	13.7	13.0	11.5
TGA test 2nd cycle	13.3	13.8	13.0	12.1

generation temperature of 700 °C are shown in Fig. 3. Sulfur loadings of CS3 and CFSs sorbents for each experiment are summarized in Table 3. In the desulfurization after reduction the CFS3 sorbent has the maximum sulfur loading of 19.8 g sulfur/100 g sorbent that is 34% higher than that of the CS3 sorbent. In the 1.5 cycle experiments the apparent sulfur loading of each sorbent decreases compared to that in the desulfurization after reduction. This is believed to be a natural phenomenon since the reduction and desulfurization reactions take place simultaneously in the 1.5 cycle reaction, i.e., the competition between weight loss and weight gain exists so the true sulfur loading cannot be seen clearly. Nevertheless, no significant change in sulfur loading between the first and second cycle indicates the relatively stable desulfurization ability of each sorbent.

Based on TGA experimental data, the effects of Fe_2O_3 content on the activation energy of reduction reaction were analyzed. The conversion of CuO-Fe_2O_3 reduction was calculated based on the following two reactions since it is not possible to directly measure the change of each composition along the reaction time.

$$CuO \rightarrow Cu + 1/2\ O_2 \tag{1}$$

$$Fe_2O_3 \rightarrow 2Fe + 3/2\ O_2 \tag{2}$$

As can be inferred from the above equations, the amount of O_2 produced by the reduction is equal to the weight loss measured by the TGA. Therefore, the conversion X will be expressed as Eq. (3).

$$X = [(100 - \text{TGA wt\%})/\text{total amount of } O_2\ (\text{wt\%})] \tag{3}$$

Many rate equations for the reduction of CuO-Fe_2O_3 sorbent might exist. Here, the power law expression for an irreversible reaction is assumed and will be expressed as Eq. (4).

$$dX/dt = k(1-X)^n \tag{4}$$

The rate constant k will be expressed as Eq. (5) from the Arrhenius equation.

$$k = A\exp(-E/RT) \tag{5}$$

where A is a preexponential frequency factor, E is an activation energy, R is a gas constant, and T is a absolute temperature.

Eq. (6) is derived from Eqs. (4) and (5).

$$dX/dt = A(1-X)^n \exp(-E/RT) \tag{6}$$

Among many methods to calculate the activation energy such as the Kissinger, Freeman-Carroll, Chatterjee-Conrad, and Friedman methods, the Chatterjee-Conrad method was applied by assuming an irreversible first order reaction. By taking a logarithm on both sides of Eq. (6), Eq. (7) is obtained.

$$\ln(dX/dt) - \ln(1-X) = -E/RT + \ln A \tag{7}$$

The activation energy can be calculated from a slope for a plot of $\ln(dX/dt) - \ln(1-X)$ vs. 1/T. Results calculated based on the Chatterjee-Conrad method are shown in Fig. 4 and Table 4. The data were taken from three experiments performed at reduction temperatures of 450, 500, and 550 °C. As can be seen from Fig. 4, the data fit the straight line within an error range of 1%, indicating that the as sumptions made in the calculation are very reasonable. As summarized in Table 4, the activation energy for reduction decreases from 149 kJ/mol to 57 kJ/mol as the amount of Fe_2O_3 in the sorbent increases. This result implies that the presence of Fe_2O_3 in a CuO-based sorbent makes the reduction proceed more easily.

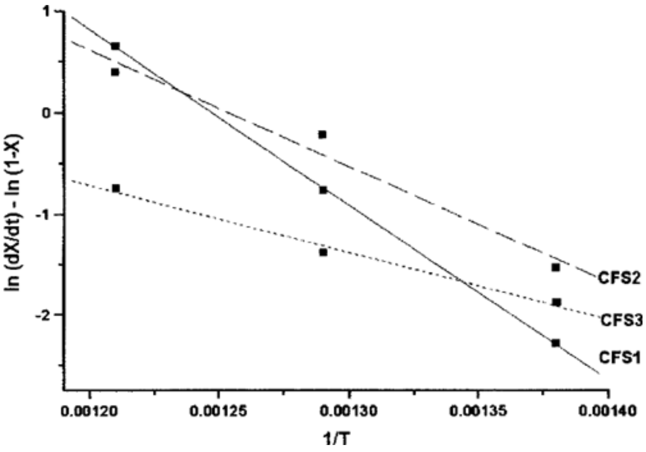

Fig. 4. Activation energy of CuO-Fe_2O_3 sorbents by Chatterjee-Conrad method.

Table 4. Activation energy of CuO-Fe_2O_3 sorbents

Sorbents	Activation energy	Error range (%)
CFS1	149 kJ/mol	±0.18
CFS2	99 kJ/mol	±0.94
CFS3	57 kJ/mol	±0.60

2. GC/Microreactor Experiments

This experiment has been performed to investigate the long-term desulfurization ability of CuO-Fe_2O_3 sorbent in a fixed bed microreactor. A breakthrough curve for CFS3 sorbent is shown in Fig. 5. The time to reach the breakthrough point initially increased as the cycle repeated, but it decreased after a certain number of cycles. It is believed that at the initial stage the sorbent forms its stable struc-

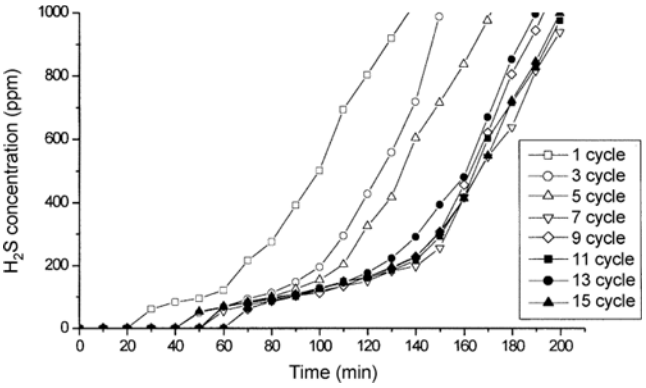

Fig. 5. Breakthrough curves of CFS3 sorbent.

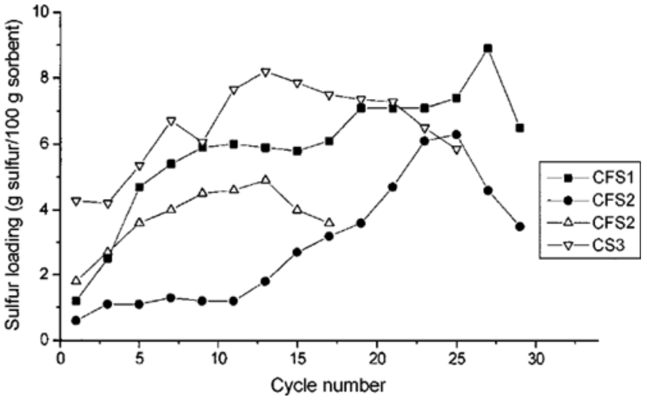

Fig. 6. Sulfur loading vs. cycle number of CuO-Fe_2O_3 sorbents.

ture resulting in the increase of breakthrough time and then it gradually loses its activity.

Fig. 6 shows the sulfur loading of CuO-Fe_2O_3 sorbent during the cyclic reactions. CFS1 sorbent, of which Fe_2O_3 content is 7.5 wt%, shows the best performance of about 8.9 g sulfur loading and its performance tends to increase with the cycle. CFS3 sorbent, which has 22.5 wt% Fe_2O_3 content, shows the best sulfur loading of about 4.6 g. While the best sulfur loading of CFS1 sorbent occurs at the 27th cycle, that of CFS3 occurs at the 13th cycle and thereafter CFS3 sorbent experienced a decrease of sulfur loading. In other words, at the experimental condition of 500 °C desulfurization temperature and 700 °C regeneration temperature, higher Fe_2O_3 content resulted in lower sulfur loading. It is well known that Fe_2O_3 has high desulfurization ability at low temperature of 400 °C. However, it has some limitations to be applied as a sorbent at higher temperature due to overreduction and formation of iron carbonates at temperatures above 550 °C and low desulfurization ability at temperatures above 700 °C [Gasper-Galvin et al., 1998]. A similar trend was observed as the content of Fe_2O_3 increased during this cycle test performed at even lower temperature of 500 °C than that reported in the literature.

XRD photographs for the sorbents used in the cycle test are shown in Fig. 7, where the additional desulfurization ability of Fe_2O_3 is confirmed. Park et al. reported that the chemical formulation of iron sulfide formed by the desulfurization reaction is FeS_2, while Tamhankar et al. reported it as $FeS_{1.1}$ [Park et al., 1992; Tamhankar et al., 1986]. However, the CuO-Fe_2O_3 sorbent with 25 wt% SiO_2 support has the FeS formulation by the desulfurization reaction.

CONCLUSION

The CFS3 sorbent of which Fe_2O_3 content is 22.5 wt% showed the lowest activation energy of 57 kJ/mol for the reduction among the CuO-Fe_2O_3 sorbents. The Chatterjee-Conrad method fitted the TGA data very well in calculating the activation energy. The activation energy decreased with the increase of Fe_2O_3 content, indicating easier reduction of sorbent. In the cyclic test the CFS1 sorbent of 7.5 wt% Fe_2O_3 showed the highest sulfur loading of 8.9 g among the CuO-Fe_2O_3 sorbents. The performance of CuO-based sorbent could be improved by the addition of Fe_2O_3.

ACKNOWLEDGEMENT

The Korea Electric Power Research Institute under the G7 program financially supported this work.

REFERENCES

Ayala, R. E., Venkataramani, V. S., Javad, A. and Hill, A. H., "Advanced Low-Temperature Sorbent," Proceedings of the Advanced Coal-Fired Power Systems '95 Review Meeting, **1**, 407 (1997).

Choi, E. Y., Lee, J. K., Park, L. K. and Park, W. H., "Removal of SO_x and NO_x from Flue Gas with Ceria," *Korean J. Chem. Eng.*, **11**, 25 (1994).

Gasper-Galvin, L. D., Atimtay, A. T. and Gupta, R. P., "Zeolite-Supported Metal Oxide Sorbents for Hot-Gas Desulfurization," *Ind. Eng. Chem. Res.*, **37**, 4157 (1998).

Javad, A., Rachid, J. S., Wangerow, J. R. and Zarnegar, M. K., "Advanced Low-Temperature Sorbents for Fluid-Bed Application," Ad-

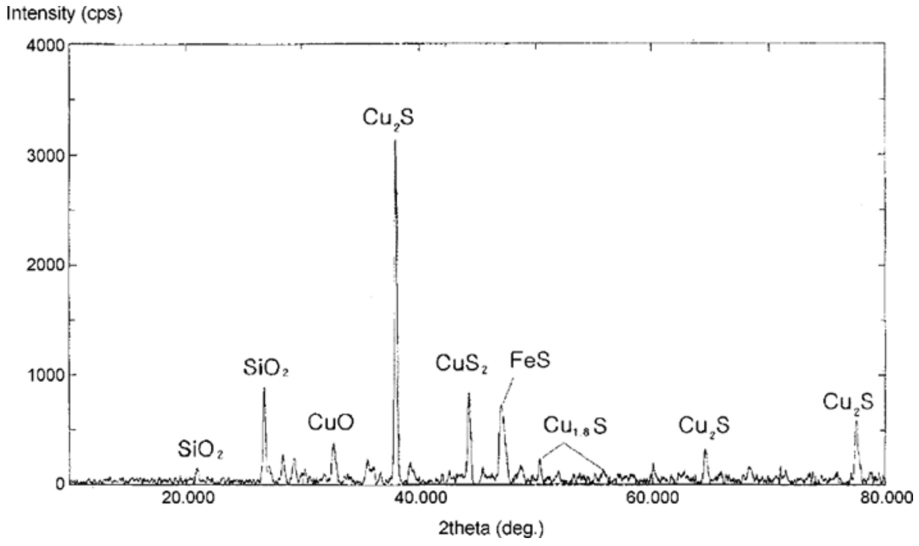

Fig. 7. XRD result of CFS3 sorbent.

anced Coal-Based Power and Environmental Systems 97 Conference July 22-24, 2A.5 (1997).

Jeon, G. S. and Chung, J. S., "Active and Selective Copper Catalysts Supported on Alkali-Doped Silica for the Dehydrogenation of Cyclohexanol to Cyclohexanone," *Korean J. Chem. Eng.*, **12**, 132 (1995).

Jeon, G. S. and Chung, J. S., "Effect of Iron on Cu/SiO_2 Catalysts for the Dehydrogenation of Cyclohexanol to Cyclohexanone," *Korean J. Chem. Eng.*, **14**, 49 (1997).

Kang, S. H., Rhee, Y. W., Han, K. H., Lee, C. K. and Jin, K. T., "A Study of Desulfurization Reaction using Zinc Titanate at High-Temperature," *HWAHAK KONGHAK*, **35**, 642 (1997).

Kyotani, T., Kawashima, H., Tomita, A., Palmer, A. and Furimsky, E., "Removal of H_2S from Hot has in the Presence of Cu-Containing Sorbents," *Fuel*, **68**, 74 (1989).

Lee, T. J., Kwon, W. T., Chang, W. C. and Kim, J. C., "A Study of Regeneration of Zinc Titanate Sorbents for H_2S Removal," *Korean J. Chem. Eng.*, **14**, 513 (1997).

Lee, Y. S., Yoo, K. O. and Gavalas, G. R., "Optimal Temperature of Fixed-Bed Reactor for High Temperature Removal of Hydrogen Sulfide," *Korean J. Chem. Eng.*, **8**, 214 (1991).

Moon, S. J. and Ihm, S. K., "Characteristics of Bimetallic Cobalt and Molybdenum Catalysts Supported on Activated Carbon or Alumina in Hydrodesulfurization," *Korean J. Chem. Eng.*, **11**, 111 (1994).

Park, D. H., Lee, Y. S., Kim, H. T. and Yoo, K. O., "Oxidative Regeneration of Sulfided Sorbent by H_2S," *HWAHAK KONGHAK*, **30**, 700 (1992).

Ryu, C. G., Wi, Y. H., Lee, C. B. and Lee, Y. K., "Removal for the Development of High Temperature Sorbent for IGCC(I)," *Chemical Industry and Technology*, **16**, 17 (1998).

Song, Y. K., Lee, K. B., Lee, H. S. and Rhee, Y. W., "Reactivity of Copper Oxide-Based Sorbent in Coal Gas Desulfurization," *Korean, J. Chem. Eng.*, **17**, 691 (2000).

Tamhankar, S. S., Bagajewicz, M. and Gavalas, G. R., "Mixed-Oxide Sorbents for High-Temperature Removal of Hydrogen Sulfide," *Ind. Eng. Chem. Process Des. Dev.*, **25**, 429 (1986).

Westmoreland, P. W. and Harrison, D. P., "Evaluation of Candidate Solid for High-Temperature Desulfurization of Low-Btu Gases," *Env. Sci. Tech.*, **10**, 659 (1976).

Yi, K. B., Choi, E. M., Song, Y. K. and Rhee, Y. W., "Low-Temperature Desulfurizing Reaction with Cu-Containing Sorbents," *HWAHAK KONGHAK*, **37**, 795 (1999).