A Study of Desulfurization Ability and Activation Energy for CuO-AgO Sorbents

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Abstract−In this study, we investigated desulfurization abilities and activation energy using TGA for CuO-AgO sorbents calcined at 700 °C. CuO was used as a main active material and AgO was used as an additive material and 25 wt% SiO_2 was used as a support material. The desulfurization reaction temperatures were 450 °C, 500 °C, and 550 °C and the regeneration reaction temperature was 700 °C. From the TGA experiments, the best sulfur loading of CAS1 sorbent containing 1 wt% AgO was about 14.95 g sulfur/100 g sorbent at 550 °C. The activation energy was calculated by the Chatterjee-Conrad method based on the TGA experiment. Desulfurization ability and activation energy of sorbent were decreased as the content of AgO increased.

Key words: Desulfurization Ability, Activation Energy, CuO-AgO Sorbent

INTRODUCTION

Recently, many developed countries have been researching techniques for the use of coal as clean energy. The IGCC (Integrated coal Gasification Combined Cycle) system has been receiving much attention due to its increased thermal efficiency and reduced environmental impact compared to conventional coal combustion plants. In the IGCC system, desulfurization is needed to protect the equipment from H_2S contained in the coal gas. In general, regenerable sorbents prepared with several metals or metal oxides have been studied to remove H_2S from the coal gas [Ryu et al., 1998; Moon and Ihm, 1994; Lee et al., 1991, 1997; Kang et al., 1997; Park et al., 1992; Jeon and Chung, 1995, 1997; Choi et al., 1994].

Westmoreland and Harrison have performed extensive thermodynamic screening tests of desulfurization potential at high temperatures for 28 basic metal oxides. Based on the experimental results, they suggested that 11 elements have thermodynamic feasibility in the range of 400-1,200 °C [Westmoreland and Harrison, 1976]. Ayala et al., investigated the thermodynamic equilibrium concentration of H_2S for several metal oxides with U-gas and Texaco-gas in the range of 350-550 °C. In their study, CuO showed the lowest H_2S equilibrium concentration, whereas copper metal showed the highest concentration. This indicates that CuO could be a very promising candidate for desulfurization sorbent if reduction of CuO to Cu is minimized in the multi-cycle reaction [Ayala 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. However, the reactivity of the physically mixed CuO sorbent showed almost the same as that of the supported sorbents [Kyotani et al., 1989]. Patrick et al. studied the decomposition temperature of the sulfur oxides

for the $CuO-Al_2O_3$ sorbents. The sulfur oxides were not decomposed below 650 °C. However, the sulfur oxides were decomposed at 700 °C [Patrick et al., 1989]. Yi et al. investigated desulfurization ability for the CuO-based sorbents with various support materials such as SiO_2, *r*-alumina, and zeolite. The sorbent using SiO_2 as support material showed the highest sulfur loading ability [Yi et al., 1999]. Song et al. investigated the optimum content of SiO_2 as support material. When the content of SiO_2 was more than 25 wt%, sorbent could maintain the structural stability in the multi-cycle experiment [Song et al., 2000]. Lee et al., investigated the activation energy in the reduction reaction of the $CuO-Fe_2O_3$ sorbents from the TGA results. The activation energy was calculated by the Chatterjee-Conrad method based on the TGA experiments [Lee et al., 2001].

In this study, CuO-AgO sorbents supported on 25 wt% of SiO_2 were prepared in order to investigate the effect of AgO content. The contents of AgO were varied as 1 wt%, 2 wt% and 3 wt%. Desulfurization ability of the sorbent was calculated from the data obtained in the TGA experiment. The activation energy was calculated by the Chatterjee-Conrad method.

METHODS

1. Sorbent Preparation

For the sorbent preparation, 25 wt% SiO_2 was used as a support material to maintain the structural stability in the cyclic test and the content of AgO was varied to 1.0 wt%, 2.0 wt% and 3.0 wt%. Based on AgO content, sorbents were named as CAS1, CAS2 and CAS3. In general, CuO sorbent has the high potential of desulfurization; however, CuO sorbent is progressively reduced to the metal copper and its desulfurization ability decreases as the experimental cycle increases. In this study, Ag, which has the lower ionization tendency than Cu, was used as an oxide form to decrease the reduction of CuO to metal copper. The composition of sorbents is summarized in Table 1. Simple mixing method was applied in preparing sorbents instead of more sophisticated methods such as precipitation

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and impregnation methods due to its economic feasibility. It has been reported that no significant differences existed in the performance of sorbents prepared by using both the simple and sophisticated methods [Kyotani et al., 1989]. Raw mixture of desired 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 tubular furnace with air atmosphere at 700 °C for 4 hours. Finally, sorbent was crushed and sieved to a size of 90-106 μm.

2. Experimental Procedure

TGA2050 (TA Instruments) was used to investigate the desulfurization ability of sorbent. Fig. 1 shows a schematic diagram of the experimental apparatus. The flow rates of reaction gases are controlled by MFCs (Mass Flow Controllers). After being mixed in a mixing tank, the gases are introduced into the TGA system. The composition of simulated gas is summarized in Table 2 and the flow

Table 1. Composition of sorbents (wt%)

Sorbents	CuO	AgO	SiO$_2$
CAS1	74	1.0	25
CAS2	73	2.0	
CAS3	72	3.0	
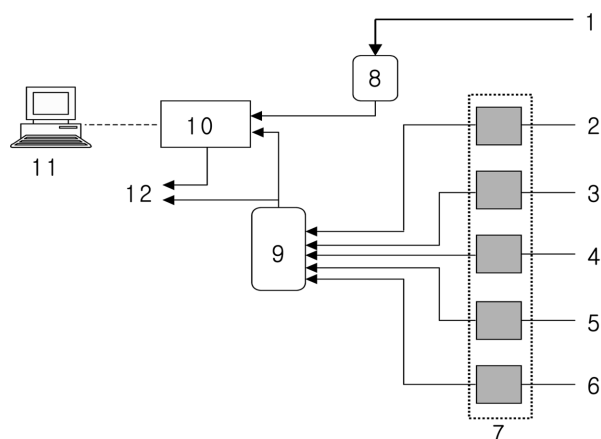
Fig. 1. Schematic diagram of experimental apparatus.

1. Ultra-pure N$_2$	7. MFC
2. H$_2$S	8. Flow meter
3. O$_2$	9. Mixing tank
4. Mixing gas	10. TGA
5. Air	11. PC
6. N$_2$	12. Vent

Table 2. Composition of simulated coal gas

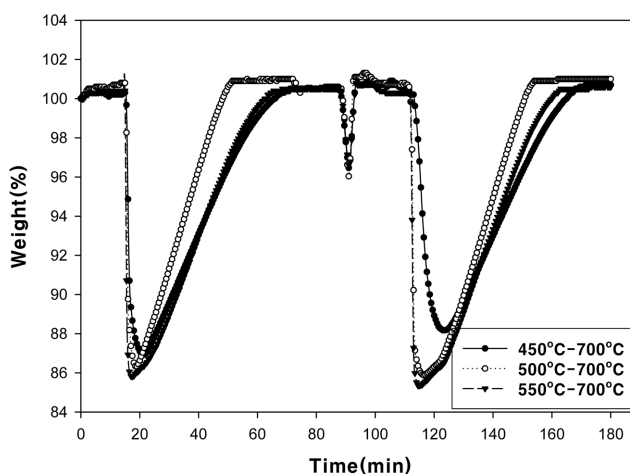| Desulfurization		Regeneration	
H$_2$	11.82%	O$_2$	5%
CO	19.18%		
CO$_2$	7.0%		
H$_2$S	0.28%	N$_2$	Balance
H$_2$O	-		
N$_2$	Balance		

rate was about 150 ml/min. About 10 mg of sorbent was used for TGA experiments. The desulfurization reaction temperatures were 450 °C, 500 °C, and 550 °C and the regeneration reaction temperature was 700 °C. The TGA experiments were performed as the 1.5 cycle reaction of desulfurization-regeneration-desulfurization. Regeneration reaction was performed after no further weight change was observed in the desulfurization reaction and then second desulfurization reaction followed after no further weight change was observed in the regeneration reaction.

In order to investigate the desulfurization characteristics of sorbents, the activation energy was calculated for the first and second desulfurization reaction by the Chatterjee-Conrad method. Each desulfurization reaction consists of reduction and sulfurization reactions.

RESULTS AND DISCUSSION

In TGA experiments, desulfurization reaction temperatures for the CAS sorbent were 450 °C, 500 °C and 550 °C and the regeneration reaction temperature was 700 °C. Lee et al. reported that CuS and Cu$_2$S were formed by the desulfurization reaction of CuO and most of the compound was Cu$_2$S type [Lee et al., 2001]. TGA experiment of CAS sorbent was performed as a reaction sequence of desulfurization - regeneration - desulfurization, and then the first and second desulfurization reactions were compared. In the desulfurization reaction, the reduction reaction rate is faster than the sulfurization reaction rate [Kang et al., 2002]. In the TGA experiment, the reduction reaction causes a weight decrease, while the sulfurization reaction causes a weight increase. In this study, desulfurization ability of sorbent was calculated from the weight difference between the lowest point and the highest point of the sulfurization reaction curve in the TGA result. Fig. 2, Fig. 3 and Fig. 4 show the TGA results of CAS sorbents with various desulfurization temperatures. Sulfur loading, which is defined as gram sulfur/100 g sorbent and indicates the desulfurization ability, is shown in Table 3.

As shown in Fig. 2, Fig. 3 and Fig. 4, the reduction reaction rate was faster than the sulfurization reaction rate regardless of AgO

Fig. 2. TGA results of CAS1 sorbent (Desulfurization: T=450 °C, 500 °C, and 550 °C; Regeneration: T=700 °C).
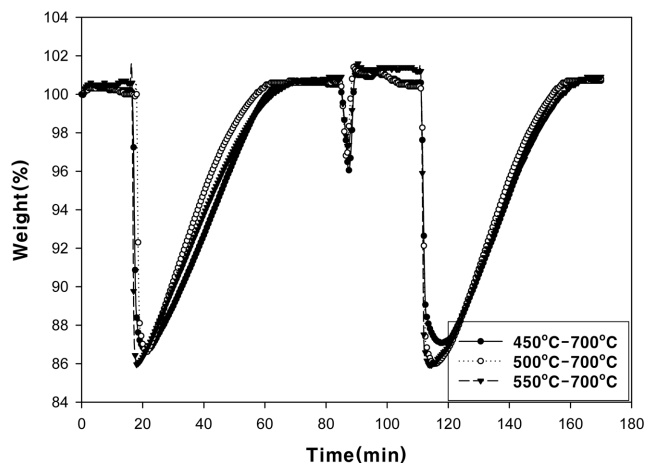
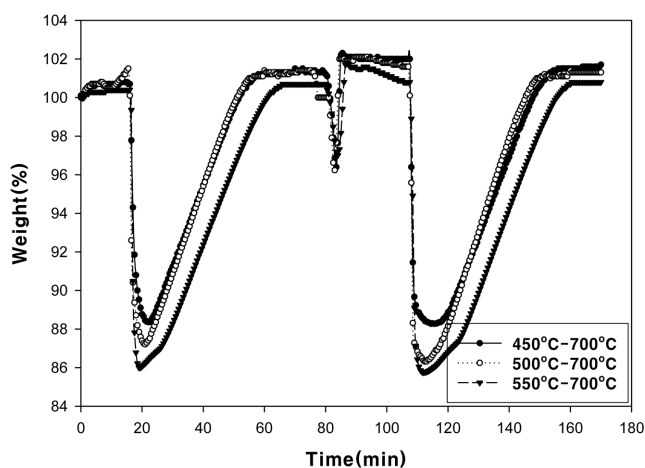**Fig. 3. TGA results of CAS2 sorbent (Desulfurization: T=450 °C, 500 °C, and 550 °C; Regeneration: T=700 °C).**

Fig. 4. TGA results of CAS3 sorbent (Desulfurization: T=450 °C, 500 °C, and 550 °C; Regeneration: T=700 °C).

Table 3. Sulfur loading of CAS sorbents for TGA 1.5 cycle test (g sulfur/100 g sorbent)

Desulfurization temperatrue	CAS1	CAS2	CAS3
450 °C	13.97	13.80	13.69
500 °C	14.58	14.32	14.20
550 °C	14.95	14.74	14.70

content and desulfurization temperature. This result indicates that the main active material, CuO, which has a faster reduction reaction rate, was overwhelming the overall reaction rate. As shown in Table 3, desulfurization ability of CAS sorbent was increased with the desulfurization temperature increase. In the same desulfurization temperature, CAS sorbent showed higher sulfur loading in the small content of AgO. The best sulfur loadings of CAS1, CAS2, and CAS3 sorbents at 550 °C were 14.95, 14.74, and 14.70 g sulfur/ 100 g sorbent, respectively.

Based on TGA experimental data, the effects of AgO content on the activation energy of first and second desulfurization reactions were analyzed. The activation energy of each desulfurization

reaction consists of the activation energy of reduction reaction and the activation energy of sulfurization reaction. In the reduction reaction, theoretical reduction capacity was calculated based on the following two reactions of Eq. (1) and (2). Theoretical sulfurization capacity was calculated based on the Cu_2S and AgS compounds.

$$CuO \leftrightarrows Cu + \frac{1}{2}O_2 \tag{1}$$

$$AgO \leftrightarrows Ag + \frac{1}{2}O_2 \tag{2}$$

The amount of reduction is equal to the weight loss and the amount of sulfurization is equal to the weight gain measured by the TGA. Therefore, the conversion X will be expressed as Eq. (3).

$$X = \frac{TGA \text{ weight change (wt\%)}}{Theoretical \text{ amount (wt\%)}} \tag{3}$$

Many rate equations for the reduction reaction and sulfurization reaction of CuO-AgO sorbent might exist. Here, the power law expression for an irreversible reaction is assumed and will be expressed as Eq. (4). The rate constant k will be expressed as Eq. (5) from the Arrhenius equation.

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

$$k = A\exp\left(-\frac{E}{RT}\right) \tag{5}$$

A is a pre-exponential frequency factor, E is an activation energy, R is a gas constant, and T is a absolute temperature.

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

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

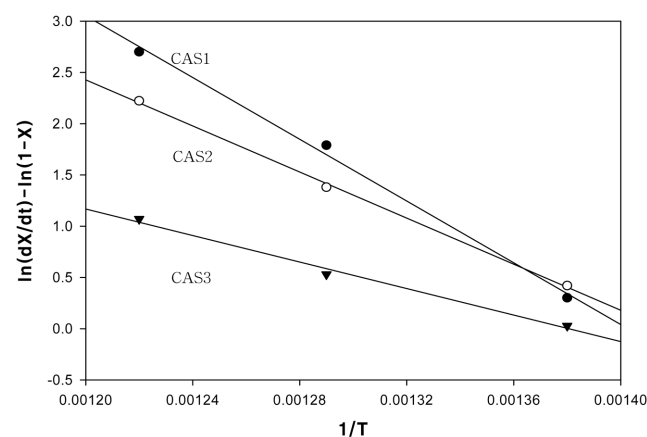$$\ln\left(\frac{dX}{dt}\right) - \ln(1 - X) = -\frac{E}{R}\frac{1}{T} + \ln A \tag{7}$$

Fig. 5. Activiation energy of CAS sorbents (first reduction).
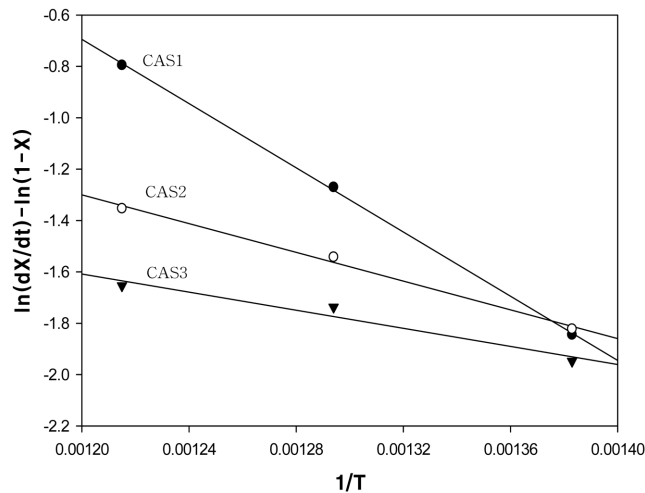
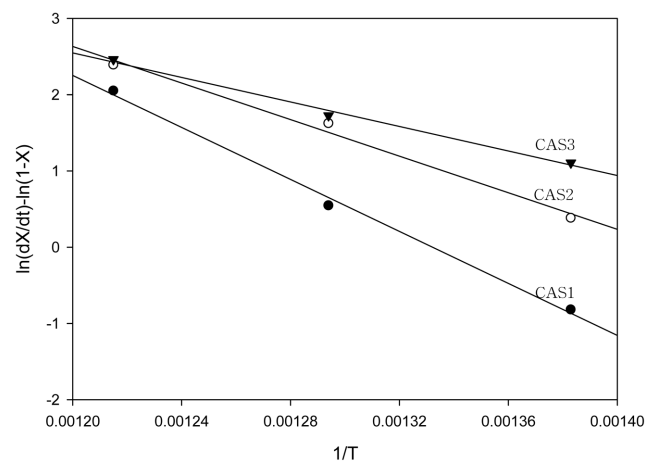Fig. 6. Activiation energy of CAS sorbents (first sulfurization).

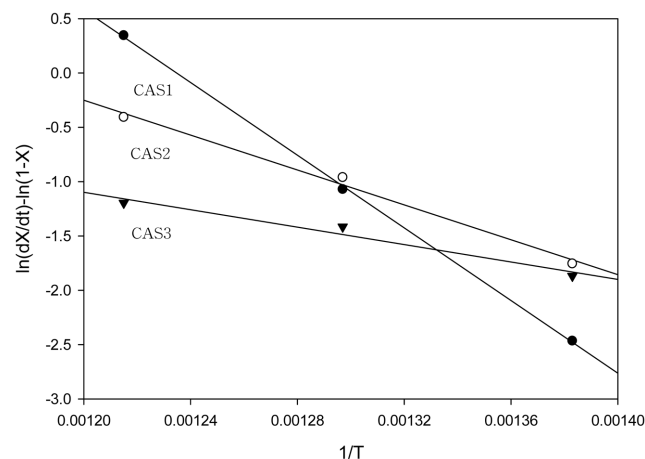Fig. 7. Activiation energy of CAS sorbents (second reduction).

Fig. 8. Activiation energy of CAS sorbents (second sulfurization).

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. 5-8. Table 4 and Table 5 show the activation energy for the first and second desulfurization

Table 4. Activation energy of CAS sorbents in the first desulfurization (kJ/mol)

Sorbents	Reduction	Sulfurization	Desulfurization	Error range (%)
CAS1	125	56	181	±1.7
CAS2	93	25	118	±1.8
CAS3	54	13	67	±2.0

Table 5. Activation energy of CAS sorbents in the second desulfurization (kJ/mol)

Sorbents	Reduction	Sulfurization	Desulfurization	Error range (%)
CAS1	142	139	281	±1.8
CAS2	100	67	167	±1.6
CAS3	67	33	100	±1.9

reactions. The data were taken from three experiments performed at desulfurization temperatures of 450, 500, and 550 °C. As shown in Fig. 5-8, the data fit the straight line within an error range of 2%, indicating that the assumptions made in the calculation are very reasonable.

Fig. 5 and Fig. 6 show the activation energy of the first reduction and sulfurization reaction. As shown in Fig. 5 and Fig. 6, the slope of the straight line is decreased as the AgO content increases. Table 4 shows the activation energy of CAS sorbents in the first desulfurization reaction. As shown in Table 4, the activation energy is decreased as the AgO content increases. When the AgO content increases from 1 wt% to 3 wt%, the activation energy of the first reduction reaction decreases from 125 kJ/mol to 54 kJ/mol and the activation energy of the first sulfurization reaction decreases from 56 kJ/mol to 13 kJ/mol. This result indicates that an increase of AgO content causes a decrease of activation energy. Lee et al. investigated the activation energy of $CuO-Fe_2O_3$ sorbents in the first reduction reaction. Their result showed that the activation energy was decreased from 149 kJ/mol to 57 kJ/mol as the Fe_2O_3 content increased from 7.5 wt% to 22.5 wt% [Lee et al., 2001]. Kang et al. investigated the activation energy of $CuO-Fe_2O_3$ sorbents in the first sulfurization reaction. In their study, the activation energy was increased from 31 kJ/mol to 73 kJ/mol as the Fe_2O_3 content increased from 7.5 wt% to 22.5 wt% [Kang et al., 2002]. Although CuO-AgO sorbents have a smaller additive content than $CuO-Fe_2O_3$ sorbents, CuO-AgO sorbents showed low activation energy in the first desulfurization, indicating that AgO is more favorable than the Fe_2O_3 as far as the reaction rate is considered only.

Fig. 7 and Fig. 8 show the activation energy of the second reduction and sulfurization reactions. As shown in Fig. 7 and Fig. 8, the slope of the straight line is decreased as the AgO content increases. This result shows the same tendency as the first desulfurization result. Table 5 shows the activation energy of CAS sorbents in the second desulfurization reaction. As shown in Table 5, the activation energy is decreased as the AgO content increases. When the AgO content increases from 1 wt% to 3 wt%, the activation energy of the second reduction reaction decreases from 142 kJ/mol to 67 kJ/mol and the activation energy of the second sulfurization reaction decreases from 139 kJ/mol to 33 kJ/mol. This result shows the same ten-

dency as the first desulfurization result.

Comparing the activation energy of the first and second desulfurization reactions, the activation energy of the first reduction and sulfurization reactions is lower than that of the second reduction and sulfurization reactions. It is speculated that this result suggests that irreducible metal oxides produced by the competitive reaction of the desulfurization reaction and unregenerated sulfides remaining after regeneration increase the activation energy of the second desulfurization reaction.

CONCLUSION

In this study, we investigated desulfurization abilities and activation energy using TGA for CuO-AgO sorbents. Desulfurization reaction temperatures were 450 °C, 500 °C and 550 °C and the regeneration reaction temperature was 700 °C. The activation energy was calculated for the 1st and 2nd desulfurization reactions by the Chatterjee-Conrad method based on the TGA result.

Desulfurization abilities of CAS sorbents were increased as the reaction temperature increased. The best sulfur loading of CAS1 sorbent containing 1 wt% AgO was about 14.95 g sulfur/100 g sorbent at 550 °C.

The activation energy of the CAS sorbents was decreased as the AgO content increased and CAS3 sorbent containing 3 wt% AgO showed lower activation energy. The addition of AgO decreased the activation energy of the CuO-based sorbents in the desulfurization reaction, indicating that AgO is a promising candidate for additive of CuO-based sorbents.

ACKNOWLEDGMENT

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