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# Reactivity of Copper Oxide-Based Sorbent in Coal Gas Desulfurization

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**Abstract**−Various CuO-based sorbents were prepared to investigate effects of sorbent ingredients such as $SiO_2$, $MnO_2$, and $MoO_3$ on desulfurization reactivity. Several candidate sorbents chosen from a TGA screening test were further tested in a microreactor system. The amount of $SiO_2$ support to minimize sintering of sorbents was 25 wt%. Sulfur loading was seriously affected by the amount of additives ($MnO_2$, $MoO_3$) in a multi-cycle test. Improvement of sulfur loading by the additives was observed in the multi-cycle test. Effects of support materials on sulfur loading were also investigated by using $SiO_2$, γ-alumina and zeolite. $SiO_2$ showed the best performance among the support candidates. The sorbent showing the best sulfur loading ability was CMS6 (CuO : $MoO_3$ : $MnO_2$ : $SiO_2$=61 : 11 : 3 : 25). Its sulfur loading reached up to 13.8 g sulfur/100 g sorbent in a multi-cycle test.

Key words: Copper Oxide-Based Sorbent, Low-Temperature Desulfurization, Additives, Support, Multi-Cycle Test

## INTRODUCTION

Cleaning technology of coal gas in the high temperature is essential for successful development of IGCC (Integrated coal Gasification Combined Cycle). High temperature cleaning technology is classified into two major processes: removing particles and desulfurization. Removing particles means removing physical impurities, and desulfurization means removing chemical impurities such as $H_2S$ in an effective way [Ryu et al., 1998; Ayala et al., 1995; Tamhankar et al., 1986; Kang et al., 1997; Lee et al., 1991].

Most sulfur compounds that exist in coal are converted into $H_2S$ during gasification, $H_2S$ is converted into $SO_2$ upon combustion in a gas turbine, and $SO_2$ becomes a precursor of acid rain that is extremely harmful to the ecosystem [Ayala et al., 1995; Lee et al., 1991; Choi et al., 1994]. Because of recent stringent regulations against air pollution, $H_2S$ should be controlled under a few tens ppmv before the gas enters into a gas turbine in the IGCC. Therefore, the development of sorbents removing $H_2S$ effectively is a key technology in the IGCC process. From 1980 to the early 1990's, the development of metal oxide removing $H_2S$ over 550 °C was greatly focused. Recent evaluation of economics for IGCC, however, showed that heat efficiency rapidly increased up to 350 °C, but in the range of 350-600 °C the increment of heat efficiency was insignificant. In addition, because of vaporization of alkali metal, it is desirable to run the process under 650 °C [Ryu et al., 1998; Javad et al., 1997]. Even though the efficiency of IGCC increases as its operation temperature increases, the optimal desulfurization temperature is known to be in the range of 350-550 °C because of limitations of equipment and alkali contents in fuel gas. There are several things to consider in selecting sorbents for IGCC such as desirable thermodynamic equilibrium, relatively high reactivity, environmental affinity and moderate cost.

Westmoreland and Harrison did desulfurization experiments systematically by using 28 elements and reported that 10 elements (Fe, Zn, Mo, Mn, V, Ca, Sn, Ba, Cu, W) were proper as sorbents in the range of 400-1,200 °C [Westmoreland and Harrison, 1976]. Ayala et al. investigated thermodynamic $H_2S$ equilibrium concentration by doing desulfurization experiments in the temperature range of 350-550 °C for the 10 elements chosen in Westmoreland and Harrison's work. Moles of solid oxides and fuel gas during sulfidation were decided based on 50% conversion. As a result, Ayala et al. found that Cu was the worst sorbent among the metals or metal oxides they tested, but CuO could keep $H_2S$ concentration lower than any other sorbents [Ayala et al., 1997]. Therefore, in our research, the sorbents containing CuO as main active material were prepared. Sulfidation and regeneration reactions of sorbents were performed in the range of 350-550 °C. Appropriate support content was decided and effects of additives and support ingredient on sulfur loading were also investigated.

## EXPERIMENT

### 1. Sorbent Preparation

$MnO_2$ and $MoO_3$ were chosen as additives and $SiO_2$, γ-alumina and zeolite were chosen as support materials. It is known that $MoO_3$ takes the role of promoter in sulfidation of CuO and $MnO_2$ inhibits vaporization of Mo in high temperature [Gasper and Washington, 1993; Moon and Ihm, 1994; Kim and Kim, 1996; Park et al., 1998; Kwak and Moon, 1999].

In this research, sorbents containing only CuO and support material were named as CS sorbents, whereas those containing CuO, $MoO_3$, $MnO_2$ and $SiO_2$ as CMS sorbents, those containing CuO, $MoO_3$, $MnO_2$ and γ-alumina as CMA sorbent, and those containing CuO, $MoO_3$, $MnO_2$ and zeolite as CMZ sorbent. A serial number was given to them according to their composition. The compositions of various sorbents are shown in Table 1. According to the literature, there is no remarkable change of desulfurization efficiency of sorbents prepared by a simple mixing method or more sophisticated methods such as impregnation and precipitation [Kyo-

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**Table 1. Composition of various sorbents (wt%)**

| Sorbents | CuO : MoO$_3$ : MnO$_2$ : Support | Support | Others : Support | CuO : MoO$_3$ : MnO$_2$ | Metal content |
|---|---|---|---|---|---|
| CS2 | 65 : 0 : 0 : 35 | SiO$_2$ | 65 : 35 | 100 : 0 : 0 | 65 |
| CS3 | 75 : 0 : 0 : 25 | SiO$_2$ | 75 : 25 | 100 : 0 : 0 | 75 |
| CS4 | 85 : 0 : 0 : 15 | SiO$_2$ | 85 : 15 | 100 : 0 : 0 | 85 |
| CS5 | 100 : 0 : 0 : 0 | None | 100 : 0 | 100 : 0 : 0 | 100 |
| CMS6 | 61 : 11 : 3 : 25 | SiO$_2$ | 75 : 25 | 81 : 15 : 4 | 61 |
| CMA1 | 61 : 11 : 3 : 25 | γ-alumina | 75 : 25 | 81 : 15 : 4 | 61 |
| CMZA | 61 : 11 : 3 : 25 | Zeolite | 75 : 25 | 81 : 15 : 4 | 61 |

**Table 2. Composition of simulated gas**

| Sulfidation | |
|---|---|
| H$_2$ | 12.1 vol% |
| CO | 19.1 vol% |
| CO$_2$ | 6.8 vol% |
| H$_2$S | For TGA : 0.3%; for GC : 1 vol% |
| H$_2$O | 10.8% |
| N$_2$ | Bal. |
| Regeneration | |
| O$_2$ | 5% |
| N$_2$ | Bal. |

tani et al., 1989]. Therefore, considering preparation cost and mass production, a simple physical mixing method was employed. Raw materials were mixed in a ball mill for 6 hours. EG (ethylene glycol) was added to make it paste form. The paste was extruded by an extruder as cylindrical pellets and placed on aluminum pan and dried at 200 °C for 4 hours. Then, it was calcined in a tubular furnace at 700 °C for 4 hours, and cooled down, crushed and sieved to desired size (92-106 µm).

**2. Experimental Procedure**

In our research, a TGA (model TGA2050, *TA Instrument*) was used to investigate weight change of sorbents during sulfidation and regeneration reactions. As shown in Fig. 1, experimental apparatus is largely divided into two parts: TGA and GC/microreactor. Gas flow rate was controlled by MFCs (mass flow controllers). The simulated coal gas composition is shown in Table 2. The mixed gas flows into TGA through the mixing tank. Water is injected by using a syringe pump. A stainless steel tube between water injection point and TGA entrance is heated by heating tape to supply water vapor to the reactor. The flow of mixed gas is vented to a fume hood until the temperature inside the chamber reaches 500 °C. After the temperature reaches 500 °C, the mixed gas flows into the TGA by manipulating valves. After reduction and sulfidation reactions, the TGA is purged by N$_2$ gas. Then, TGA temperature is set to 700 °C, which is the regeneration temperature. After the temperature reaches 700 °C, regeneration gas is introduced into the TGA. As described above, a cycle of sulfidation and regeneration is repeated.

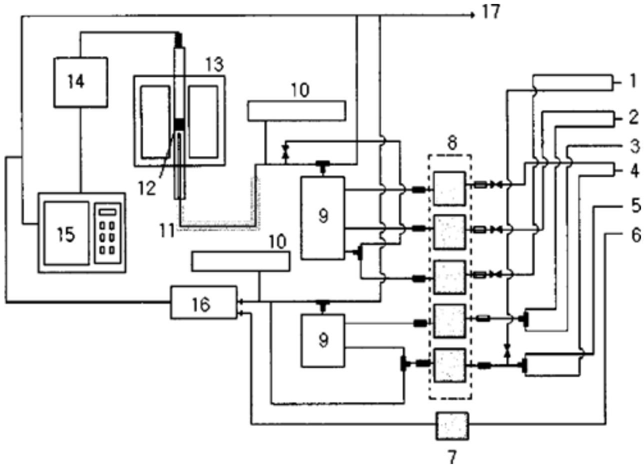

**Fig. 1. Schematic diagram of experimental apparatus.**

1. N$_2$
2. H$_2$S
3. SO$_2$
4. Mixing gas
5. Air
6. N$_2$
7. Flowmeter
8. MFC
9. Mixing tank
10. Syringe pump
11. Heating tape
12. Sample
13. Microreactor
14. Water trap
15. GC
16. TGA
17. Vent

The GC used in our research is a Young-In M600D model (*Young-In Ind. Korea*) with TCD. The sorbent, 3 g, is loaded in a microreactor, which has 2.54 cm diameter and is made of quartz where a stratum is placed inside for quartz wool to support sorbents. Composition of simulated gas for GC/microreactor experiment is similar to that for TGA. The difference of gas composition between TGA test and GC/microreactor test is the concentration of H$_2$S; 1% of H$_2$S is used in order to save time in a multi-cycle reaction. A small sized refrigerator is used to condense water in the exit gas from the microreactor.

## RESULTS AND DISCUSSION

### 1. Determination of Support Content

Sorbents with various silica content were studied to determine appropriate silica content. Results of the TGA test are shown in Fig. 2. Desulfurization reaction of copper oxide-based sorbent consisted of two steps: reduction of copper oxide and sulfidation of copper with H$_2$S. So, a typical result of the TGA test of copper oxide-based sorbent shows a decrease of weight first by fast reduction reaction and then shows weight gain by sulfidation. The changes of sulfur loading of sorbents are shown in Table 3. As shown in Fig. 2 and Table 3, sulfur loading of sorbents in the first cycle mainly depends upon metal content; sulfur loading increased as metal oxide con-

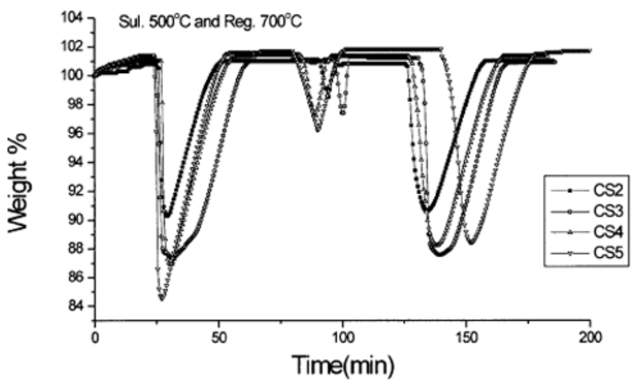

**Fig. 2. TGA curves of CS2, 3, 4 and 5 (1.5 cycle).**

**Table 3. Effects of support content on sulfur loading (TGA)**

| Sorbents | CuO (%) | $SiO_2$ (%) | 1st cycle sulfur olading (%) | 2nd cycle sulfur loading (%) |
|---|---|---|---|---|
| CS2 | 65 | 35 | 10.7 | 10.4 |
| CS3 | 75 | 25 | 13.6 | 13.3 |
| CS4 | 85 | 15 | 14.5 | 13.1 |
| CS5 | 100 | 0 | 17.2 | 13.3 |

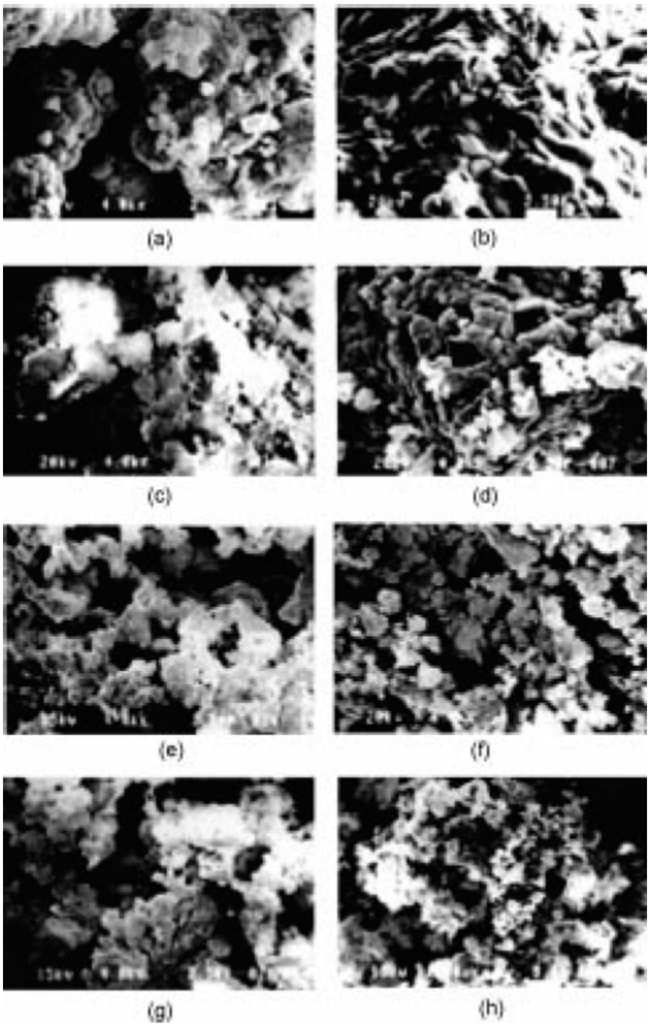

**Fig. 3. SEM photographs of sorbents (×4000).**
(a) CS5 fresh, (b) CS5 after 30 cycle, (c) CS4 fresh, (d) CS4 after 20 cycle (e) CS3 fresh, (f) CS3 after 20 cycle, (g) CS2 fresh, (h) CS2 after 20 cycle.

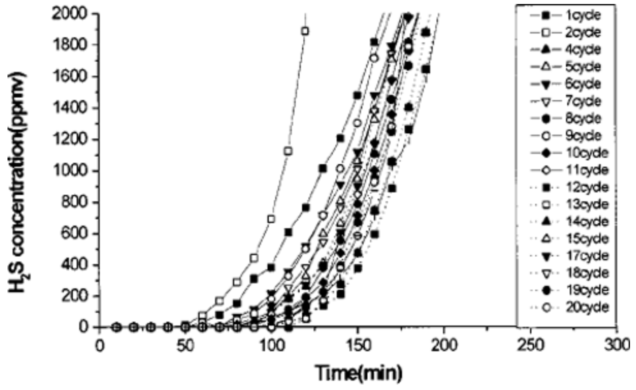

**Fig. 4. Breakthrough curves of CS3.**

tents increased. But in the second, sulfur loading does not depend upon metal content. It shows a decreasing tendency. Sulfur loading of CS5 decreased by 22.7% and that of CS4 decreased by 9.7%. As compared to CS5 and CS4, CS3 and CS2 decreased by 2.2% and 2.8%, respectively. Fig. 3 shows SEM photographs of sorbents (fresh and reacted). As shown in Fig. 3, in the case of CS5 and CS4 sorbents pore structure was destroyed by sintering. However, in the case of CS3 and CS2, there is no remarkable structural change between fresh sorbent and reacted sorbent. CS2 and CS3 have similar pore structure. These results suggest that about 25% of silica would be necessary to maintain the structural integrity and the reactivity of copper oxide-based sorbents.

## 2. Effects of Additives

The changes of sulfur loading of sorbents with various metal oxide contents and fixed silica content (25%) were studied to investigate effects of additives on sulfidation reaction. Sulfur loading increased as metal oxide contents increased. But the increment of sulfur loading by sulfidation of $MoO_3$ was negligible [Yi, 1999]. Though it was expected that $MoO_3$ would take a role of promoter for sulfidation, a promoting effect of $MoO_3$ was not observed in this short-term sulfidation/regeneration reaction in TGA test. Therefore, to investigate effects of $MoO_3$ and $MnO_2$ on sulfidation in multi-cycle reactions, CMS6 was tested in the GC/microreactor system and its result was compared to that of CS3. The reason why CMS6 was chosen was that CMS6 showed better sulfur loading than any other sorbent containing $MoO_3$ and $MnO_2$ in TGA screening test. As shown in Table 1, CS3 does not contain any additives besides CuO and $SiO_2$. Fig. 4 shows a breakthrough curve of CS3, where breakthrough time increases as the cycle number increases. Since microreactor tests were carried out in a fixed bed reactor, there was a considerable amount of unreacted copper oxide in the early cycles. As the cycle was repeated, sorbent could provide more accessible reactive sites to reaction gas. Sulfur loading of sorbent was calculated by counting out $H_2S$ concentration until it reached 50 ppmv. Sulfur loadings of CMS6 and CS3 sorbent in multi-cycle are shown in Fig. 5. As shown in Fig. 5, sulfur loadings of CS3 before the fifth cycle are larger than those of CMS6. This is well

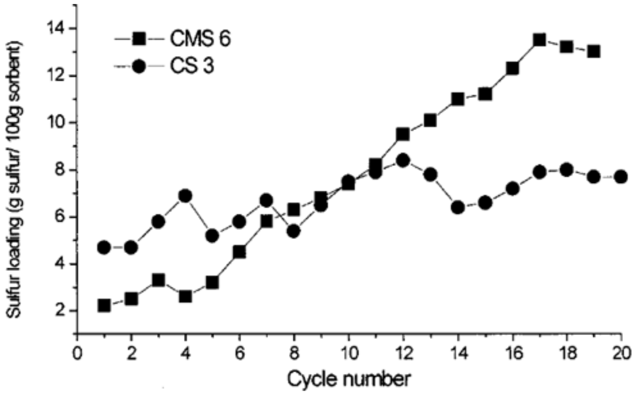

**Fig. 5. Sulfur loadings of CMS6 and CS3 in multi-cycle reactions (basis ; 50 ppmv $H_2S$ out).**

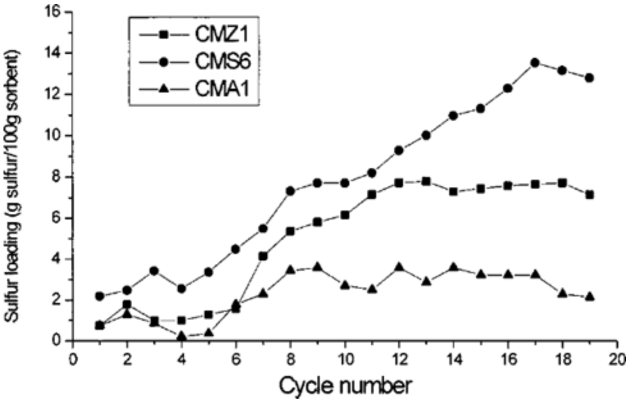

**Fig. 7. Sulfur loadings of CMS6, CMA1 and CMZ1 in multi-cycle reactions.**

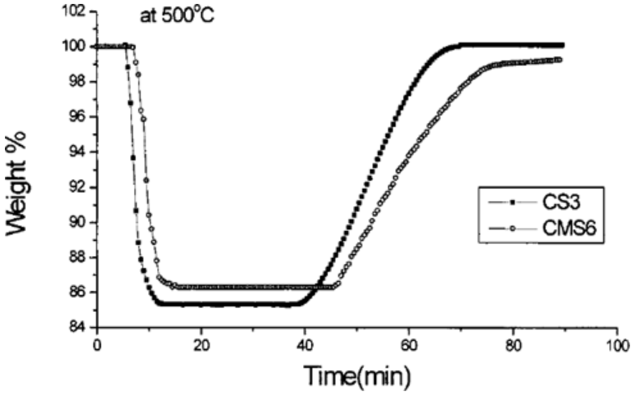

**Fig. 6. Weight gain of CS3 and CMS6 in TGA test.**

matched with the result of the TGA test as shown in Fig. 6, because CS3 contains more metal oxide contents than CMS6. In the TGA experiment for CMS6, the sorbent was sulfided with simulated coal gas after it had been fully reduced without $H_2S$. From this TGA experiment the maximum sulfur loading and maximum extent of reduction were obtained. We found that CuO is reduced almost 100% to Cu. However, it is hard to know whether the reduced form of CuO is metallic Cu, $Cu^+$ or $Cu^{2+}$ at present since any morphological experiment data are not available at the point when the sorbent was fully reduced. As the cycle number increased, sulfur loadings of CMS6 became larger than those of CS3. CS3 sorbent seemed to be fully activated at around the 12th cycle (sulfur loading was 8.2 g sulfur/100 g sorbent), but CMS6 sorbent was fully activated at around the 17th cycle (sulfur loading was 13.8 g sulfur/100 g sorbent). Sulfur loading of CS3 before the 5th cycle reached to twice that of CMS 6, but sulfur loading of CMS 6 after 15th cycle, when sorbents were fully activated, was almost twice that of CS3. Even though CS3 contained more CuO than CMS6, it showed poor sulfur loading. This implies that additives ($MnO_2$, $MoO_3$) would promote sulfur loading ability.

**3. Effects of Support Material on Sulfur Loading**

To investigate effects of support material on sulfur loading, sorbents with different support materials were prepared. Because CMS6 showed better sulfur loading ability than any other sorbent in the TGA screening test [Yi, 1999], CMA1 and CMZ1 were prepared with same metal oxide content ratio and different support material, γ-alumina and zeolite, respectively. Sulfur loadings of CMS6, CMA1 and CMZ1 are shown in Fig. 7. Even though CMA1 sorbent had same composition of metal oxide, it showed very poor sulfur loading. It was fully activated at around the 8th cycle. Because support material of CMA1 was γ-alumina and showed poor performance, it is clear that $SiO_2$ is more suitable for support material than γ-alumina. In the case of CMZ1, sulfur loading before 7th cycle was quite low like CMA1, and it increased until the cycle number reached 13. When CMZ1 was fully activated, its sulfur loading did not reach that of CMS6. Its sulfur loading ranged between that of CMA1 and that of CMS6. The reason for this observation is that zeolite consists of alumina and $SiO_2$.

## CONCLUSION

Various sorbents were prepared by simple mixing method. CuO was used as the main active material, $MnO_2$ and $MoO_3$ were used as additives, and $SiO_2$, γ-alumina and zeolite were used as support materials. TGA screening test, GC/microreactor multi-cycle reaction tests and sorbent characterization were carried out to find the most desirable sorbent composition. About 25% of support content is required to maintain reactivity and structural stability of sorbent for multi-cycle reaction. The promoting effect of $MoO_3$ on sulfidation was not observed in the TGA experiment, but it became significant in multi-cycle reactions. In the GC/microreactor multi-cycle reaction, $H_2S$ breakthrough time of CMS 6 sorbent increased as the cycle number increased due to stabilization of the sorbent structure. The sorbent was fully activated and stabilized after 15th cycles and its sulfur loading was 13.8%. The presence of additives ($MoO_3$ and $MnO_2$) enhanced sulfur loading.

Composition of metal oxides was fixed to that of CMS6 since it gave the highest sulfur loading among the CMS series sorbents. CMA1 sorbent supported on g-alumina showed poor sulfur loading ability through the whole cycles. CMZ1 sorbent supported on zeolite showed poor sulfur loading ability during first few cycles and was fully stabilized after the 13th cycle. Based on sulfur loadings observed in multi-cycle reaction, $SiO_2$ was the most appropriate support material for the sorbent containing CuO as main active material.

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