

Reactivity of Copper Oxide-Based Sorbent in Coal Gas Desulfurization

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(Received 21 June 2000 • accepted 11 October 2000)

Abstract—Various CuO-based sorbents were prepared to investigate effects of sorbent ingredients such as SiO₂, MnO₂, and MoO₃ on desulfurization reactivity. Several candidate sorbents chosen from a TGA screening test were further tested in a microreactor system. The amount of SiO₂ support to minimize sintering of sorbents was 25 wt%. Sulfur loading was seriously affected by the amount of additives (MnO₂, MoO₃) 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 SiO₂, γ -alumina and zeolite. SiO₂ showed the best performance among the support candidates. The sorbent showing the best sulfur loading ability was CMS6 (CuO : MoO₃ : MnO₂ : SiO₂ = 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 H₂S 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 H₂S during gasification, H₂S is converted into SO₂ upon combustion in a gas turbine, and SO₂ 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, H₂S 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 H₂S effectively is a key technology in the IGCC process. From 1980 to the early 1990's, the development of metal oxide removing H₂S 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 sys-

tematically 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 H₂S 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 H₂S 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

MnO₂ and MoO₃ were chosen as additives and SiO₂, γ -alumina and zeolite were chosen as support materials. It is known that MoO₃ takes the role of promoter in sulfidation of CuO and MnO₂ 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, MoO₃, MnO₂ and SiO₂ as CMS sorbents, those containing CuO, MoO₃, MnO₂ and γ -alumina as CMA sorbent, and those containing CuO, MoO₃, MnO₂ 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

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 μ m).

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

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.

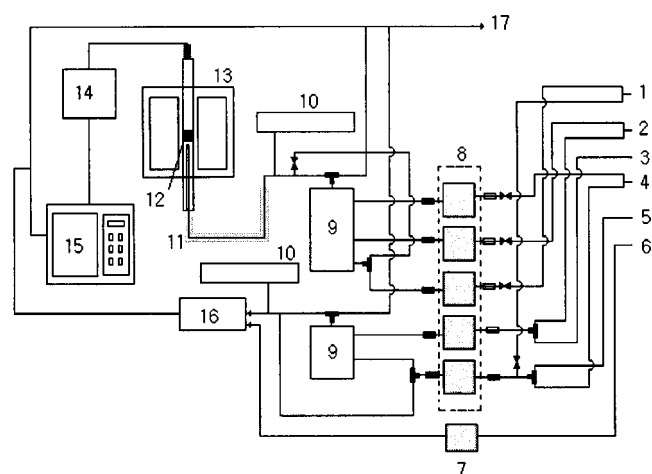
hood until the temperature inside the chamber reaches 500 °C. After the temperature reaches 500 °C, the mixed gas flows into the TGA by manipulating valves. After reduction and sulfidation reactions, the TGA is purged by N₂ gas. Then, TGA temperature is set to 700 °C, which is the regeneration temperature. After the temperature reaches 700 °C, regeneration gas is introduced into the TGA. As described above, a cycle of sulfidation and regeneration is repeated.

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 H₂S; 1% of H₂S 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 H₂S. 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. 1. Schematic diagram of experimental apparatus.**

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

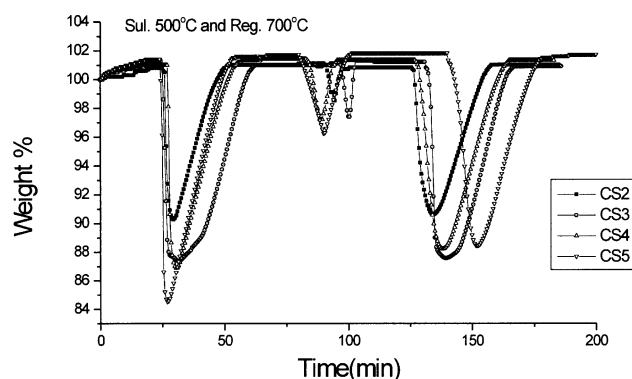


Fig. 2. TGA curves of CS2, 3, 4 and 5 (1.5 cycle).

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

Sorbents	CuO (%)	SiO ₂ (%)	1 st cycle sulfur loading (%)	2 nd 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

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 MoO₃ was negligible [Yi, 1999]. Though it was expected that MoO₃ would take a role of promoter for sulfidation, a promoting effect of MoO₃ was not observed in this short-term sulfidation/regeneration reaction in TGA test. Therefore, to investigate effects of MoO₃ and MnO₂ 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 MoO₃ and MnO₂ in TGA screening test. As shown in Table 1, CS3 does not contain any additives besides CuO and SiO₂. 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

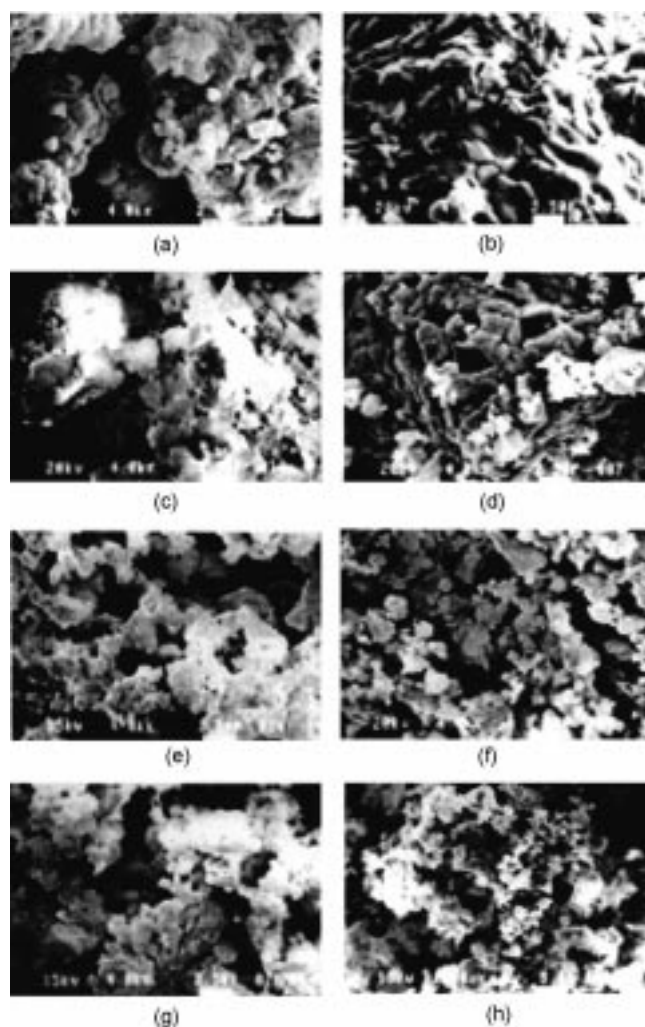


Fig. 3. SEM photographs of sorbents (x4000).

(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.

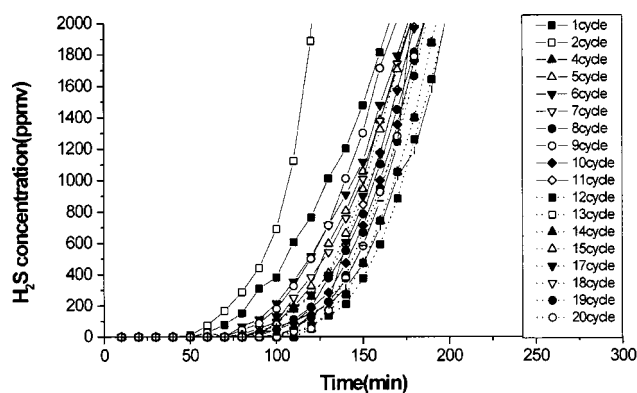


Fig. 4. Breakthrough curves of CS3.

calculated by counting out H₂S 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

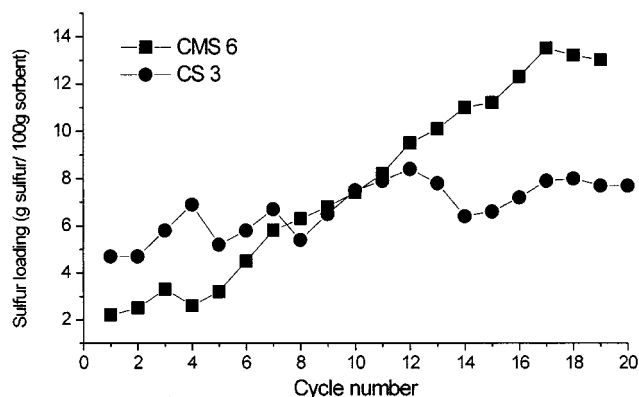


Fig. 5. Sulfur loadings of CMS6 and CS3 in multi-cycle reactions (basis ; 50 ppmv H_2S out).

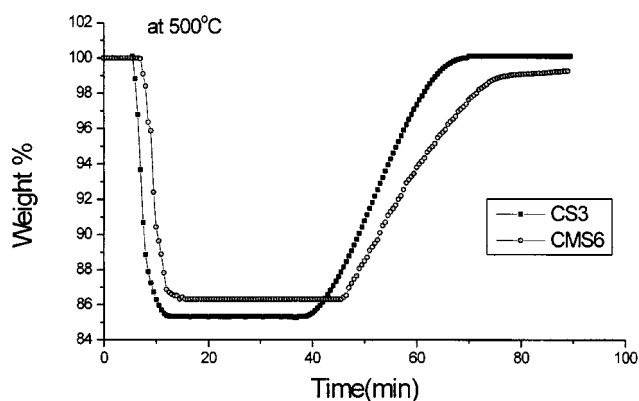


Fig. 6. Weight gain of CS3 and CMS6 in TGA test.

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

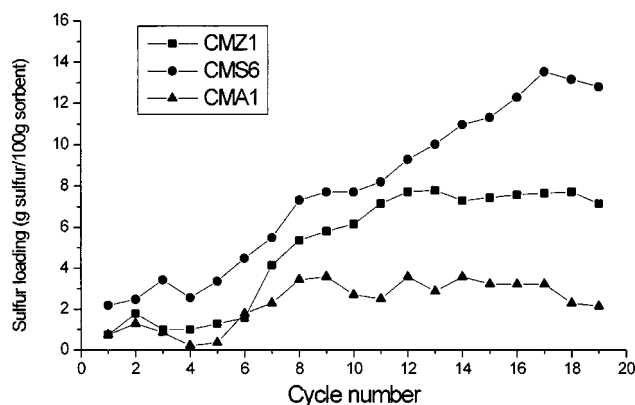


Fig. 7. Sulfur loadings of CMS6, CMA1 and CMZ1 in multi-cycle reactions.

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 γ -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.

ACKNOWLEDGEMENT

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

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