

EFFECT OF SULFIDATION/OXIDATIVE REGENERATION CYCLE ON THE SOLID STRUCTURAL CHANGES OF SORBENT FOR HIGH-TEMPERATURE REMOVAL OF H₂S

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Abstract – In order to investigate the effects of sulfidation/oxidative regeneration cycle on the change of structural properties and removal capacity of sorbent, sulfidation/regeneration cycle was carried out up to 15 times in a fixed-bed reactor. The effluent gases from the fixed-bed reactor were analyzed by gas chromatography, and XRD, SEM, and liquid nitrogen physisorption method were used to characterize the reacted sorbents. The sorbent treated first sulfidation/regeneration cycle exhibited maximum specific surface area and the highest H₂S removal capacity. Hysteresis of adsorption isotherm of the regenerated sorbent reflected the growth of pores of fresh sorbent and pore size distribution confirmed this fact. Furthermore constant H₂S removal capacity was maintained up to 15 times of sulfidation/regeneration cycle.

Key words: Structural Properties, Sulfidation/Oxidative Regeneration, H₂S Removal Capacity

INTRODUCTION

Nowadays, environmental pollution has been serious global problem and legal regulation like Clean Air Act has been reinforced.

The objective of this study is removal of H₂S, one of the most dangerous air pollutants. Although conventional process called cold scrubbing technique is effective for the removal of H₂S, it has demerits; loss of sensible heat of the gas and costly wastewater treatment [Lew et al., 1989]. As a alternative, high temperature desulfurization method using metal oxide and mixed metal oxide sorbents has been accomplished to enhance the efficiency of H₂S removal from the hot coal-derived gas [Cannon and Denbigh, 1957; Tamhankar et al., 1981, 1986; Yumura and Furimsky, 1986; Yoo, 1986; Lee et al., 1991, 1995; Choi, 1992]. These metal oxide/mixed metal oxide sorbents must have not only high H₂S removal capacity but also good regenerability. Many investigators reported valuable results about regeneration of sulfided sorbents [Griendley et al., 1981; Harrison et al., 1989; Park et al., 1992; Lee et al., 1994, 1995].

In our previous studies, optimal reaction conditions for sulfidation and the effects of regeneration temperature, oxygen concentration and Fe₂O₃ additive on the oxidative regeneration of sulfided sorbent with O₂ have been determined [Lee et al., 1991, 1994, 1995; Choi et al., 1992; Park et al., 1992].

In the present study, the effect of structural changes of the sorbent was investigated due to sulfidation/oxidative regeneration cycle on the H₂S removal capacity of ZnO-5 at % Fe₂O₃ sorbent with the aids of SEM, BET, XRD.

It was reported that ZnO was a very effective sorbent for H₂S removal and regeneration, but it has a big flaw to vaporize elemental zinc above 600°C [Lew et al., 1989]. Addition of 5

at % Fe₂O₃ was made to accelerate the initial rate of sulfidation, to prevent vaporization of ZnO to elemental zinc and sintering of sorbent due to sulfidation [Yoo et al., 1995]. The expression at % means that the percent by weight of mixture divided by atomic weight.

EXPERIMENTAL SECTION

1. Preparation of Sorbent and Sulfidation/oxidative Regeneration Cycle

Our recent research [Lee et al., 1995] explained the preparation method of the metal oxide sorbent and sulfidation/oxidative regeneration cycle experiment in detail.

2. Characterization of Sorbent

The fresh, sulfided, and regenerated sorbents were characterized by several bulk, and surface analysis techniques.

(1) X-ray diffraction (XRD, Rigaku RAD-C) was performed for identification of crystalline phases and solid products in the metal oxide sorbent.

(2) Scanning electron microscopy (SEM, JEOL-JSM-3 SCF) was used to observe the surface morphology of sulfided and regenerated sorbents.

(3) Liquid nitrogen physisorption method (Micrometric ASAP 2000) was applied to investigate the adsorption isotherm and structural properties (specific surface area, total pore volume, and average pore diameter).

RESULTS AND DISCUSSION

Table 1 showed change of structural properties of reacted sorbents obtained from the liquid nitrogen physisorption method. Sulfidation made specific surface area and total pore volume decrease, and oxidative regeneration made these properties increase. This is a common phenomenon in gas-solid reaction. It

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Table 1. Liquid N₂ physisorption analysis data

| Sorbent | Surface area (m ² /g) | Total pore volume (cc/g) × 10 ³ | Average pore diameter (Å) |
|-------------------------|----------------------------------|--|---------------------------|
| fresh | 2.65 | 2.15 | 32.51 |
| 1st Sulfidation | 2.52 | 1.97 | 69.46 |
| 1st Regeneration | 33.72 | 270.40 | 320.30 |
| 2nd Sulfidation | 4.25 | 8.63 | 81.14 |
| 2nd Regeneration | 5.97 | 41.90 | 318.23 |
| 4th Sulfidation | 5.27 | 24.22 | 162.26 |
| 4th Regeneration | 9.79 | 74.05 | 302.58 |
| 6th Sulfidation | 3.87 | 7.48 | 77.24 |
| 6th Regeneration | 11.87 | 101.50 | 341.98 |
| 8th Sulfidation | 4.08 | 10.97 | 107.49 |
| 8th Regeneration | 11.09 | 95.13 | 343.25 |
| 10th Sulfidation | 2.78 | 7.37 | 77.92 |
| 10th Regeneration | 10.27 | 78.62 | 306.33 |
| 15th Sulfidation | 4.00 | 10.39 | 103.72 |

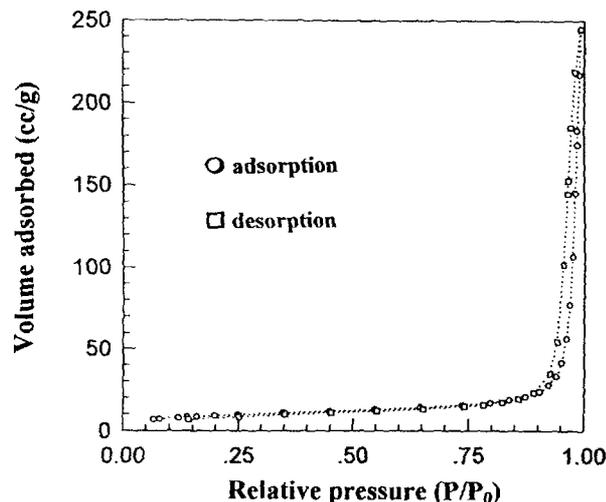
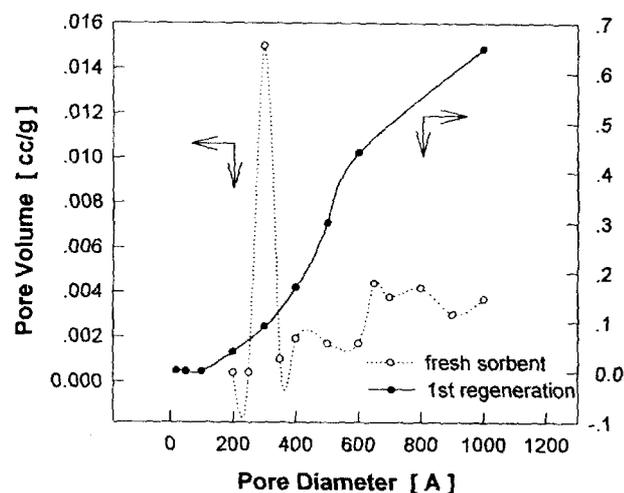
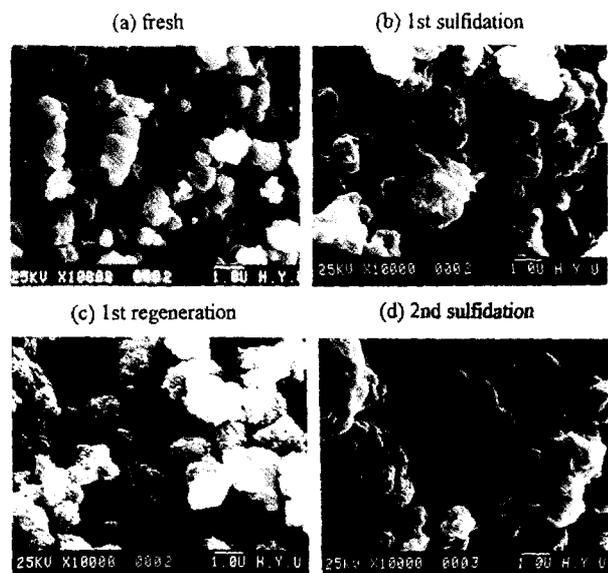
was reported that average pore diameter increased after sulfidation and decreased after oxidative regeneration [Harrison et al., 1989], although, the reverse was occurred in this study. Although the appropriate reason was not clear, one reason is considered to be very high average pore diameter of the first regenerated sorbent. Especially, the sorbent treated by first sulfidation/regeneration cycle exhibited the highest specific surface area. This is a reason of better H₂S removal capacity of regenerated sorbent than that of fresh sorbent. This fact is similar to that of Harrison et al. [1989].

Fig. 1 showed the liquid nitrogen adsorption isotherm of the regenerated sorbent. This isotherm belongs to Type IV isotherm and hysteresis, which did not detect in the fresh sorbent, represented the pore growth of fresh sorbent. It was found that adsorption isotherms of sulfided sorbents were alike regardless of number of sulfidation, and those of regenerated sorbents were similar regardless of number of regeneration. This means that sulfidation and regeneration did not change the pore structure of sulfided and regenerated sorbent, respectively.

Fig. 2 represented the pore size distribution of fresh and regenerated sorbents. The small pores of fresh sorbent (about 300 Å) disappeared and the growth of pore size due to regeneration was confirmed

Fig. 3 and Fig. 4 depicted SEM morphology of reacted sorbents. Photos of sulfided sorbents showed coagulation of sorbent grains and this agglomeration decreased specific surface area of the sorbent. Surface morphology of sulfided sorbents was alike regardless of number of sulfidation cycle. This fact is coincidence with the conclusion resulted from similar adsorption isotherm of the sulfided sorbents. On the contrary, the photos of the regenerated sorbents showed cracks between the sorbent grains and this cracks provided high specific surface area and, thus, high H₂S removal capacity than that of fresh sorbent.

Conversion-time curves for sulfidation were represented in Fig. 5 and Fig. 6. The definition of conversion was $1 - C_A/C_{A0}$ where C_A is the effluent concentration of H₂S at arbitrary time and C_{A0} is the inlet H₂S concentration. The removal capacity of H₂S, calculated from the area under the time-conversion curves, was shown in Fig. 7. The removal capacity of sorbents was

**Fig. 1. Liquid N₂ adsorption isotherm of regenerated sorbent.****Fig. 2. Pore size distribution of fresh and regenerated sorbents.****Fig. 3. SEM morphology of reacted sorbents.**

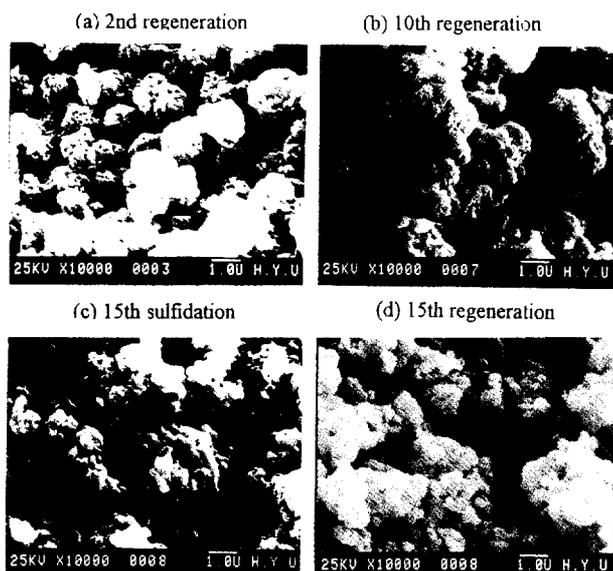


Fig. 4. SEM morphology of reacted sorbents.

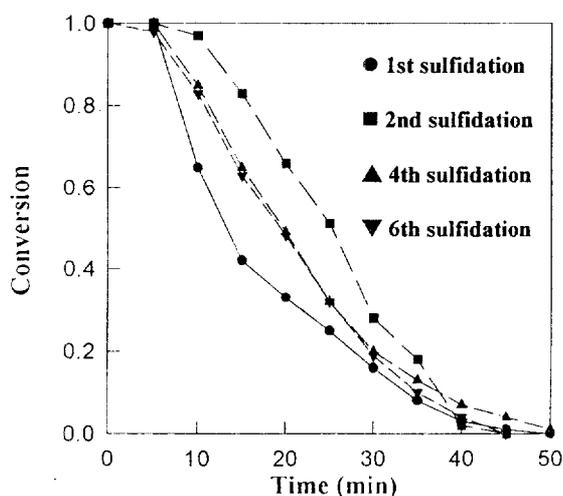


Fig. 5. Conversion vs. time curves for sulfidation.

considered to be constant, although, first sulfidation/regeneration treated sorbent exhibited the highest removal capacity. This was due to high specific surface area of the sorbent. In general the reactivity of solid reactant in gas-solid reaction is high as specific surface area of solid reactant is large and first sulfidation/regeneration treated sorbent had the highest specific surface area. Furthermore, the removal capacity of regenerated sorbent was higher than that of fresh sorbent and this is also considered to be caused high specific surface area.

XRD analysis for sulfided and regenerated sorbents confirmed the complete sulfidation and regeneration.

CONCLUSIONS

Sulfidation decreased specific surface area and pore volume and oxidative regeneration increased those properties.

The sorbent treated first sulfidation/regeneration cycle ex-

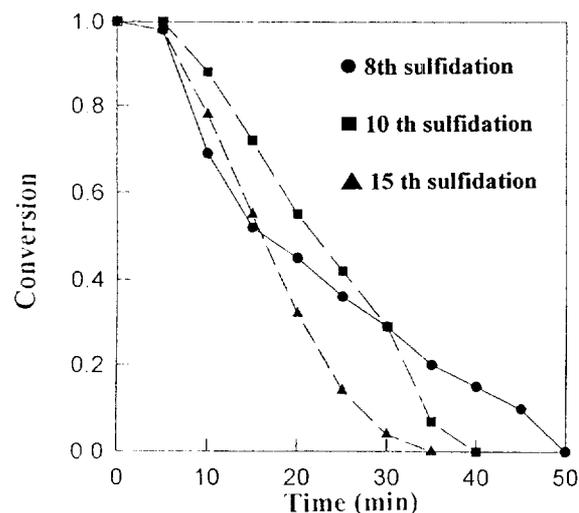
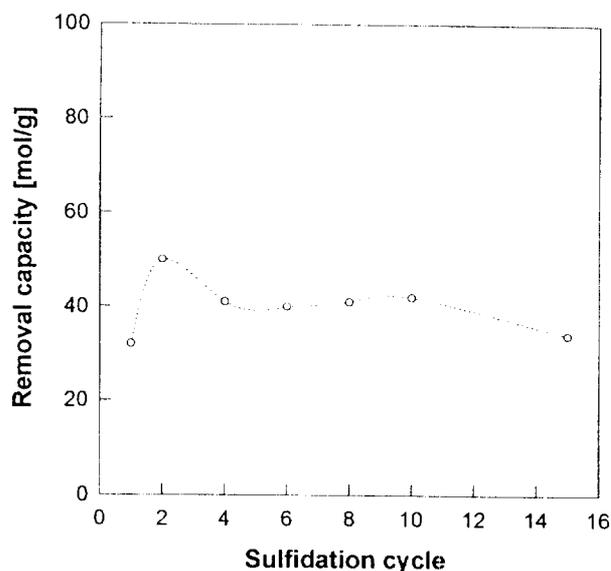


Fig. 6. Conversion vs. time curves for sulfidation.

Fig. 7. H₂S removal capacity for sulfidation cycle No.

hibited the highest specific surface area and thus the highest H₂S removal capacity.

The removal capacity of regenerated sorbents was higher than that of fresh sorbent and was considered to be constant regardless of sulfidation/regeneration cycle except first sulfidation/regeneration cycle.

REFERENCES

- Cannon, K. J. and Denbigh, K. G., "Studies on Gas-Solid Reactions-I. The Oxidation Rate of Zinc Sulphide", *Chem. Eng. Sci.*, April/May, 145 (1957).
- Choi, Y. J., Lee, Y. S., Kim, H. T. and Yoo, K. O., "A Study on the Fixed-Bed Reactor for High Temperature Removal of Hydrogen Sulfide-Effect of Packing Height, Particle Size of Sorbent and Fe₂O₃ Additive", *Hwahak Konghak*, 30(4), 433 (1992).

- Grindley, T. and Steinfeld, G., "Development and Testing of Regenerable Hot Coal Gas Desulfurization Sorbents", *Techn. Prog. Rep.*, DOE/MC/16545-1125, DOE Contract No. DE-AC21-81MC16545 (1981).
- Lee, S., Jotimurugesan, K. and Stephanopoulos, M. F., "High Temperature H₂S Removal from Fuel Gases by Regenerable Zinc Oxide-Titanium Dioxide Sorbents", *Ind. Eng. Chem. Res.*, **28**(5), 535 (1989).
- Lee, Y. S., Kim, H. T. and Yoo, K. O., "Effect of Ferric Oxide on the High-Temperature Removal of Hydrogen Sulfide over ZnO-Fe₂O₃ Mixed Metal Oxide Sorbent", *Ind. Eng. Chem. Res.*, **34**, 1181 (1995).
- Lee, Y. S., Park, D. H., Kim, H. T. and Yoo, K. O., "Oxidative Regeneration of Sulfided Sorbent by H₂S without Emission of SO₂", *Korean J. Chem. Eng.*, **12**(1), 23 (1995).
- 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**(4), 214 (1991).
- Lee, Y. S. and Yoo, K. O., "Effect of Ferric Oxide on the Oxidative Regeneration of Sulfided ZnO-Fe₂O₃ Sorbent", *Hwahak Konghak*, **32**(3), 506 (1994).
- Park, D. H., Lee, Y. S., Kim, H. T. and Yoo, K. O., "Oxidative Regeneration of Sulfided Sorbent by H₂S", *Hwahak Konghak*, **30**(6), 700 (1992).
- Sa, L. N., Focht, G. D., Ranade, P. V. and Harrison, D. P., "High Temperature Desulfurization Using Zinc Ferrite: Solid Structural Property Change", *Chem. Eng. Sci.*, **44**(2), 215 (1989).
- Tamhankar, S. S., Bagajewicz, Gavalas, G. R., Sharma, P. K. and Stephanopoulos, M. F., "Mixed Oxide Sorbents for High Temperature Removal of Hydrogen Sulfide", *Ind. Eng. Chem. Process Des. Dev.*, **25**(2), 429 (1986).
- Tamhankar, S. S., Hasatani, M. and Wen, C. Y., "Kinetic Studies on the Reaction Involved in the Hot Gas Desulfurization Using a Regenerable Iron Oxide Sorbent I. Reduction and Sulfidation of Iron Oxide", *Chem. Eng. Sci.*, **36**, 1181 (1981).
- Yoo, K. O., "Additive Effect of Sorbents for Removal of Hydrogen Sulfide", *Res. Inst. Ind. Sci. Rep., Hanyang Univ.*, **25**, 245 (1986).
- Yumura, M. and Furimsky, E., "Comparison of CaO, ZnO, and Fe₂O₃ as H₂S Adsorbents at High Temperatures", *Ind. Eng. Chem. Process Des. Dev.*, **24**(4), 1165 (1985).