

High Temperature Desulfurization over ZnO-Fe₂O₃ Mixed Metal Oxide Sorbent

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ZnO-Fe₂O₃ 複合金屬 酸化物을 利用한 高溫에서의 黃化水素 除去에 關한 研究

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국 문 초 록

ZnO-Fe₂O₃ 복합금속 산화물 흡착제가 황화수소 제거능이나 황화된 흡착제의 산화적 재생반응에 미치는 영향을 고찰하였다. Zinc ferrite 흡착제가 가장 높은 황화수소 제거능을 나타내었고 혼합한 Fe₂O₃ 흡착제는 황화반응 도중 SO₂의 생성을 촉진시킴을 알 수 있었다. 또한 황화반응의 결과로 생성되는 금속 황화물들이 H₂S 열분해의 촉매로 작용하였으며 H₂는 Fe₂O₃의 함량이 증가할수록 더 많이 발생하였다. 산화적 재생반응의 결과로부터 ZnS를 제외하고 Fe₂O₃를 혼합한 흡착제는 모두 잘 재생됨을 알 수 있었다. 또한 산화적 재생반응 도중 생성될 수 있다고 보고된 zinc sulfate는 생성되지 않았다. 그리고 SO₂ 발생 곡선의 형태나 완전재생에 소요되는 시간을 기준으로 판단해 볼때 Fe₂O₃의 혼합량의 변화는 산화적 재생반응에 별다른 영향을 미치지 않음을 알 수 있었다.

Keywords : High temperature desulfurization, ZnO-Fe₂O₃ mixed metal oxide sorbent, oxidative regeneration, XRD analysis, thermal decomposition of H₂S.

Introduction

Recently, water and environmental pollution becomes serious social problem and high technology makes this pollution accelerate. Hydrogen sulfide, the main subject of our research, is one of the most dangerous air pollutant like SO_x and NO_x.

The major contaminant in coal gasification is H₂S, which is very toxic, hazardous and extremely corrosive. Therefore, control of hydrogen sulfide to a safe level is essential. Although commercial desulfurization process called liquid scrubbing is effective for removal of H₂S, it has drawbacks, the loss of sensible heat of the gas and costly wastewater treatment.¹⁾ Many investigations are

carried out about high-temperature removal of H₂S in hot coal-derived gas using metal oxide or mixed metal oxide sorbents.²⁻¹⁰⁾ It was reported that ZnO was very effective sorbent for H₂S removal, but it has big flaw to vaporize elemental zinc above 600°C.¹⁾ As alternative, metal oxides such as CaO, Fe₂O₃, TiO₂ and CuO were added to ZnO.²⁾ Especially, different results are reported for Fe₂O₃ additive. Tamhankar *et al.*³⁾ reported SiO₂ with 45 wt% Fe₂O₃ sorbent is favorable for removal of H₂S and regeneration. Whereas Focht and Harrison *et al.*⁴⁾ reported that zinc ferrite (ZnFe₂O₄), which is composed of ZnO and Fe₂O₃, sorbent was suitable for H₂S removal. From our previous results, we found out that Fe₂O₃ additive accelerated initial rate of sulfidation²⁾ and prevented structural change of sorbent due to sulfidation.⁵⁾

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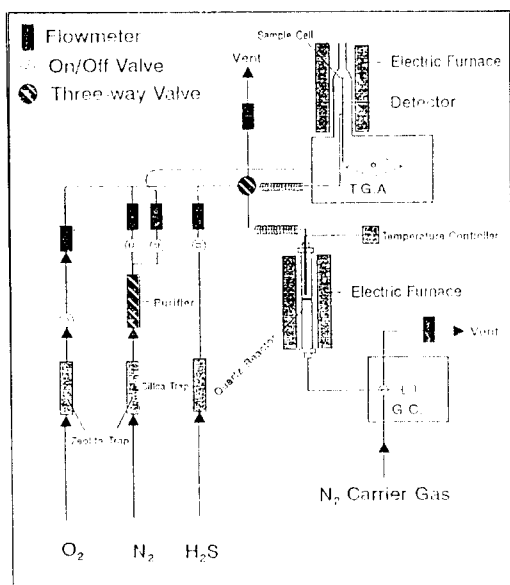


Fig. 1. Schematic diagram of experimental apparatus.

In present research, therefore, removal capacity of H₂S over ZnO-Fe₂O₃ mixed metal oxide sorbents and oxidative regeneration of sulfided sorbents were investigated.

Materials and Methods

1. Preparation of sorbent

Sorbent was prepared by a conventional method of synthesizing highly porous metal oxides.¹¹⁾ According to this method, an aqueous solution containing the metal salts in desired proportion, and an organic polyfunctional acid with at least one hydroxy and one carboxylic function, was rapidly dehydrated under vacuum at about 70°C. The resulting amorphous solid foam was calcined at 800°C to form the mixed metal oxide phase. The crystallized oxides thus formed were homogeneous and highly porous.

2. Sulfidation and oxidative regeneration experiment

The sulfidation and oxidative regeneration were performed in the reactor system shown in Fig. 1. The reactor consisted of a quartz tube, 1 cm i.d.×45 cm length, mounted vertically inside an

Table 1. Experimental conditions of sulfidation and oxidative regeneration

	Sulfidation	Oxidative regeneration
Temperature	650°C	750°C
Gas composition	H ₂ S : 2 vol% N ₂ : 98 vol%	O ₂ : 10 vol% N ₂ : 90 vol%
Total gas flow rate	200 ml/min	100 ml/min
Particle size	60~80 mesh	60~80 mesh
Packing amount	0.2 g	0.2 g
Pressure	1 atm	1 atm

electric furnace and instrumented with a Chromel-Alumel thermocouple moving inside a quartz thermowell (0.3 cm i.d) attached by quartz fritted wool. Different gases from regulated cylinders passed through purifiers and then through calibrated flow meters into a common gas line. The gas mixture then passed through the reactor in the downward direction and the lines leading to the reactor were heated. The effluent gases exited through fixed-bed reactor were analyzed by a G.C. equipped with TCD and 8 ft×1/8 in o.d. Chromosil 310 column (supplied by Supelco) operating at 50°C.

Yoo *et al.*^{12,13)} reported optimal temperature for the sulfidation and regeneration. Therefore sulfidation and oxidative regeneration was carried out at 650°C, 750°C, respectively. Table 1 describes experimental conditions.

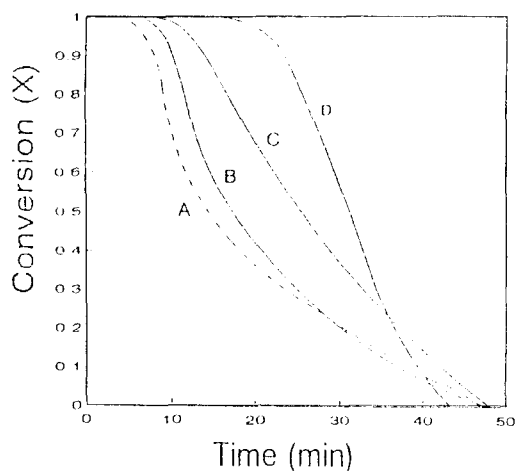
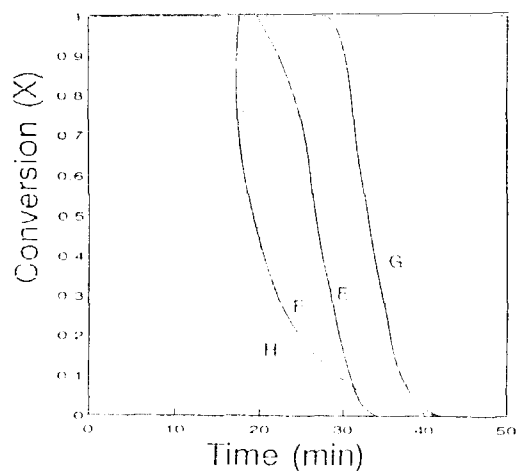
Because of difficulty of G.C. calibration for SO₂ and H₂, the numeric values of SO₂ and H₂ in Y-axis were obtained by peak area recorded and total SO₂ uptake was the product of flow rate of gas, SO₂ uptake (peak area of G.C. recorder) and time on stream.

3. XRD analysis

X-ray diffraction (XRD, Rigaku RAD-C) analysis was performed for the identification of crystalline phases in the mixed metal oxides. The scanning speed and diffraction angle were 2°/min and 20~50°, respectively.

Table 2. Results of XRD analysis and complete regeneration time (min) for various sorbents

Sorbent	ZnO (wt%)	Fe ₂ O ₃ (wt%)	Fresh	Sulfided	Regenerated	Time (min)
A	100	0	ZnO	ZnS, ZnO	ZnO, ZnS	13
B	97	3	ZnO, ZnFe ₂ O ₄	ZnS, ZnO	ZnO, ZnFe ₂ O ₄	26
C	95	5	ZnO, ZnFe ₂ O ₄	ZnS	ZnO, ZnFe ₂ O ₄	23
D	90	10	ZnO, ZnFe ₂ O ₄	ZnS	ZnO, ZnFe ₂ O ₄	22
E	70	30	ZnO, ZnFe ₂ O ₄	ZnS	ZnO, ZnFe ₂ O ₄	25
F	50	50	ZnO, ZnFe ₂ O ₄	ZnS, FeS _x	ZnO, ZnFe ₂ O ₄	25
G	30	70	ZnFe ₂ O ₄ , Fe ₂ O ₃	FeS _x , ZnS	ZnFe ₂ O ₄ , Fe ₂ O ₃	25
H	0	100	Fe ₂ O ₃	FeS _x	Fe ₂ O ₃	22

**Fig. 2.** Conversion vs. time curves for sulfidation of sorbents (A~D).**Fig. 3.** Conversion vs. time curves for sulfidation of sorbents (E~H).

Results and Discussion

1. XRD analysis

Results of XRD analysis and complete regeneration time for various sorbents are represented in Table 2. All of the sorbents were highly crystalline compounds. When ferric oxide (Corundum) was added above 3 wt%, it was found the coexistence of zinc ferrite (ZnFe₂O₄) phase with spinel structure and ZnO phase with hexagonal structure. As more ferric oxide was added, the characteristic peak of ZnO at $2\theta=36^\circ$ was decreased, whilst that of ZnFe₂O₄ at $2\theta=35^\circ$ was increased. There was double phases crystallographic structure change from ZnO-ZnFe₂O₄ phase to ZnFe₂O₄-

Fe₂O₃ phase. To investigate the change of lattice parameter due to additive for the case of 1~2.0 wt% of Fe₂O₃, cell volume of hexagonal ZnO was calculated and no significant difference was confirmed.

2. H₂S removal capacity

Conversion-time curves for sulfidation were depicted in Fig. 2 and 3. H₂S removal capacity, Q_r , defined as H₂S removal amount (the area under conversion-time curve) per unit gram of sorbent, was depicted in Fig. 4. Gradual increase of removal capacity of H₂S was confirmed till sorbent D. Although no special trends for H₂S removal was examined for sorbents E~H, sorbent G, composed

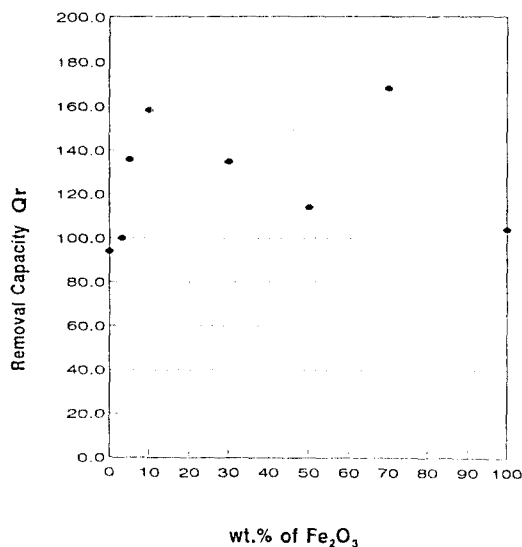


Fig. 4. H₂S removal capacity for various sorbents.

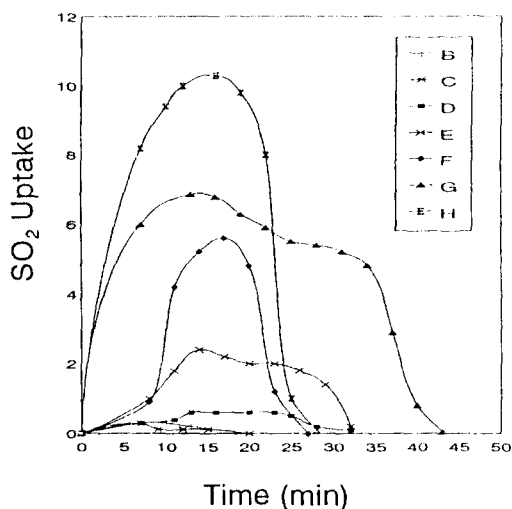


Fig. 5. SO₂ uptake produced during the sulfidation.

of ZnFe₂O₄ mainly, had the highest removal capacity of H₂S.

3. SO₂ uptake during sulfidation

Fig. 5 represented SO₂ uptake produced during the sulfidation. There was no emission of SO₂ for pure ZnO sorbent. Above 3 wt% Fe₂O₃ addition, SO₂ started to emit. As ferric oxide increased, SO₂ emitted gradually and the time for SO₂ generation

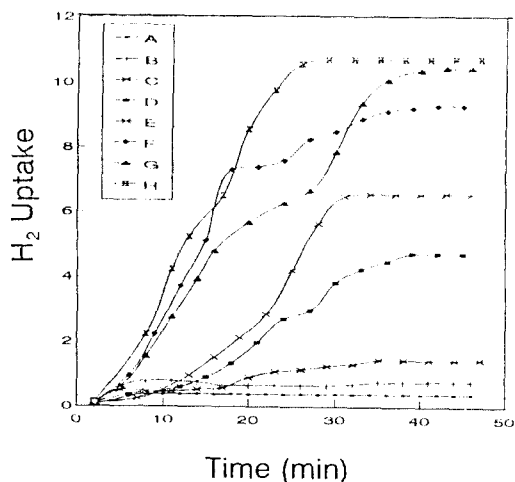


Fig. 6. H₂ uptake produced during the sulfidation.

was long. This indicated that sorbents containing Fe₂O₃ removed H₂S in the form of SO₂ and Yumura and Furimsky¹⁴⁾ reported the generation of SO₂ during the removal of H₂S over Fe₂O₃ sorbent. We also carried out sulfidation over sorbents containing 1, 2 wt% Fe₂O₃ because general XRD analysis did not detect compound of which composition was below 3 wt% and little emission of SO₂ was confirmed. Therefore we concluded that zinc ferrite made SO₂ emitted during the removal of H₂S. By the way, Harrison *et al.*⁴⁾ reported zinc ferrite was excellent sorbent for H₂S removal and we mentioned similar result in Fig. 2. But they executed sulfidation with the aids of thermogravimetric method and as a result they did not analyze effluent gases, especially SO₂. Consequently it was considered that zinc ferrite was not best sorbent for the removal of H₂S.

4. H₂ uptake during sulfidation

Fig. 6 illustrated H₂ uptake generated during the sulfidation. This phenomenon indicated thermal decomposition of H₂S into H₂ and elemental sulfur. Fukuda *et al.*¹⁵⁾ and Chivers *et al.*¹⁶⁾ reported this occurrence in the presence of metal sulfide. Behie *et al.*¹⁷⁾ interpreted this fact thermodynamically but very low conversion of H₂S (about 5% at 650°C) was also reported.¹⁵⁾ H₂ uptake was more as ferric oxide increased. This was caused

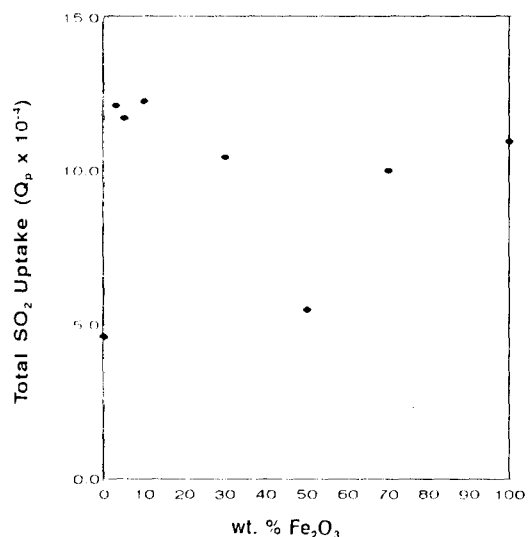


Fig. 7. Total SO₂ uptake, Q_p, produced during the oxidative regeneration.

by the strong catalytic effect of FeS_x, which was produced from the sulfidation of Fe₂O₃, than that of ZnS.¹⁴⁾

5. SO₂ uptake during oxidative regeneration

Fig. 7 represented total SO₂ produced, Q_p, generated during oxidative regeneration of sulfided sorbents. The numeric values of Q_p were calculated from time vs. conversion curves. For oxidative regeneration of ZnS (Table 2, A), the time was very short, approximately 13 min, and SO₂ uptake decreased drastically. From XRD analysis, complete regeneration was not occurred for pure ZnS. This can be interpreted as follows. First, for the sulfidation of pure ZnO sorbent containing no Fe₂O₃, severe structural changes due to sulfidation acted as O₂ diffusion barrier¹³⁾ and this brought about long reaction time. For this case the tailing of curve of SO₂ uptake must be examined. Second hydrodynamic behavior like channeling made flow path of gaseous reactant change. Especially oxidative regeneration of sulfided sorbents was high exothermic reaction¹³⁾ and high exothermic reaction heat accelerated structural change causing uneven penetration of gaseous reactant.¹⁸⁾ Stroch and Balakotaiah¹⁹⁾ described reaction-induced flow maldistribution mathematically and this maldistri-

bution leads to hot spots in reactor and spread in the residence time. Considering reaction time and shape of SO₂ uptake curve, the second was more appropriate. It was reported that when severe structural change existed, complete regeneration of sulfided sorbent can not be achieved.⁷⁾ Furthermore the variation of amount of Fe₂O₃ added did not affect oxidative regeneration significantly.

Zinc sulfate reported to be generated during oxidative regeneration^{7,8)} was not detected.

Conclusions

From the experimental results of sulfidation and oxidative regeneration in the fixed-bed reactor, we obtained the following conclusions.

1) When ferric oxide was added to the zinc oxide phase, double phase crystallographic structure was occurred. We found that zinc ferrite phase with spinel structure yielded high H₂S removal capacity and Fe₂O₃ added removed H₂S in the form of SO₂ during the sulfidation. Hydrogen resulted from the thermal decomposition of H₂S in the presence of metal sulfides was increased as ferric oxide was increased.

2) Complete regeneration was occurred for all the sorbents containing Fe₂O₃ except pure ZnS. Zinc sulfate reported to be generated during the oxidative regeneration was not detected. On the basis of SO₂ uptake curve and the time required for complete regeneration, we concluded that the amount of Fe₂O₃ added did not affect the oxidative regeneration significantly.

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