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OXIDATIVE REGENERATION OF SULFIDED SORBENT BY H_2S WITHOUT EMISSION OF SO_2

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Abstract – Much SO_2, another perilous air pollutant, was emitted during the oxidative regeneration of sulfided sorbent by H_2S. In order to prevent emission of SO_2, we carried out oxidative regeneration with the physical mixture of CaO and sulfided sorbent and investigated the effect of regeneration temperature and oxygen concentration on the reactivity of CaO with SO_2. The effluent gases were analyzed by G.C. and the properties of sorbent were characterized by XRD, SEM, TG/DTA and EPMA. Deterioration of reactivity of CaO with SO_2 resulted in increment of emission of SO_2 due to the structural changes of CaO above 750℃ and that at 850℃ was more severe. Furthermore EPMA and XRD analysis revealed that product layer diffusion through the solid product, $CaSO_4$, was the rate limiting step for CaO sulfidation. The reaction of CaO with SO_2 was first order approximately and that was accelerated by high O_2 concentration.

Key words: Oxidative Regeneration of Sulfided Sorbent, SO_2 Removal, EPMA, Product Layer Diffusion Control

INTRODUCTION

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

The target of our research is removal of H_2S, one of the most dangerous air pollutant. This gas is very toxic, poisonous, and corrosive. Therefore control of hydrogen sulfide to a safe level is essential. Although conventional process called cold scrubbing technique is effective for removal of H_2S, it has drawbacks, loss of sensible heat of the gas and costly waste water treatment. As a alternative, high temperature desulfurization using metal oxide or mixed metal oxide sorbents [1-5] has been carried out to enhance the efficiency of H_2S removal from hot coal-derived gas. These metal oxide/mixed metal oxide sorbents must have not only high H_2S removal capacity but also good regenerability. Many investigators [6-10] also reported valuable results about regeneration of sulfided sorbents.

Our previous researches reported optimal reaction conditions for sulfidation [2-3] as well as effect of regeneration temperature and oxygen concentration for oxidative regeneration of sulfided sorbent with O_2 [4]. But during the oxidative regeneration, another toxic air pollutant, SO_2 was produced.

Therfore, in order to prevent emission of SO_2, we accomplished oxidative regeneration with the physical mixture of sulfided sorbent and CaO, which has been reported as excellent sorbent for SO_2 [11-17] and investigated the effect of regeneration temperature and oxygen concentration on the reactivity of CaO. The characterization of reacted sorbent was carried out with the aids of XRD, SEM, TG/DTA and EPMA.

EXPERIMENTAL

1. Preparation of Sorbent

Sorbent was prepared by a conventional method of synthesizing highly porous metal oxides [18]. According to this method, an aqueous solution containing the metal salts in desired portion, and an organic polyfunctional acid were rapidly dehydrated under vacuum at about 70℃ for 24 hours. The resulting amorphous solid foam was calcined at 800℃ for 5 hours to form the mixed-metal oxide. The crystallized mixed metal oxide thus formed were homogeneous and highly porous.

The fresh sorbent for H_2S removal was ZnO-5 at.% Fe_2O_3. The ferric oxide was added to prevent the vaporization of ZnO to elemental zinc [5], to increase the mechanical strength and to accelerate the initial rate of ZnO sulfidation [1].

CaO (Hiyashi Co.) for SO_2 removal was calcined at 1000℃ for 5 hrs and crushed to 16-35 mesh.

2. Characterization of Sorbent

The fresh and sulfided sorbent and CaO sorbent were characterized by several bulk and surface techniques.

(1) X-ray diffraction (XRD: Rigaku RAD-C) was performed for identification of crystalline phases and solid products.

(2) Scanning electron microscopy (SEM: Jeol, JSM-3 SCF) was used to observe the surface morphology.

(3) Thermogravimetric analysis and differential thermal analysis (TG/DTA: SEICO 320) were used to investigate the variation of property due to heating.

(4) Electroprobe microanalysis (EPMA: Jeol JXA 8600) was used to observe spatial distribution of sulfur within the sorbent.

3. Apparatus and Procedure

The reaction experiments were performed in the fixed-bed reactor system shown in Fig. 1. The fixed-bed reactor consisted of a quartz tube, 1 cm i.d.×45 cm length (30 cm from entrance to fritted quartz wool), was mounted vertically inside an electric furnace and instrumented with a Chromel-Alumel thermocoulpe in thermowell located by fritted quartz wool. Different gases from regulated cylinders passed through purifiers and then through calibrated flow meters into a common SUS gas line. The gas mixture then passes through the reactor in the downward direction

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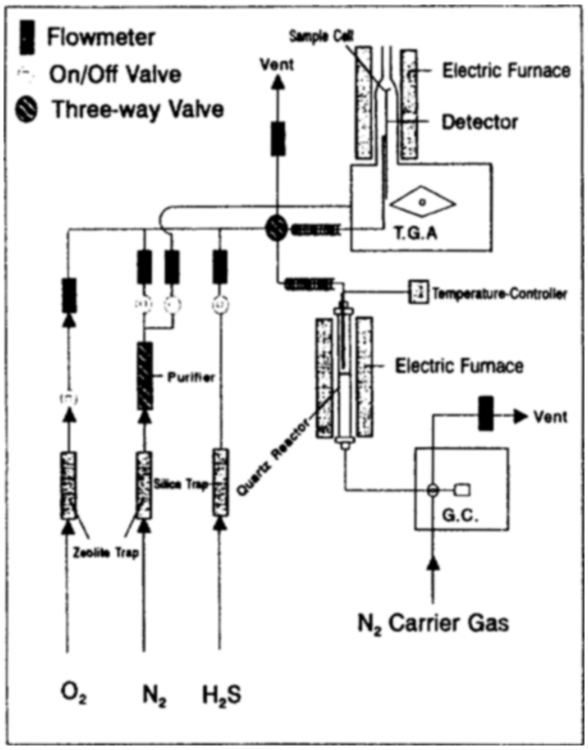

Fig. 1. Schematic diagram of experimental apparatus.

Table 1. Experimental conditions of sulfidation and oxidative regeneration with CaO

	Sulfidation	Oxidative regeneration with CaO
Temperature	650℃	650-850℃
Gas composition	H_2S: 2 vol% N_2: 98 vol%	O_2: 3-21 vol% N_2: 79-97 vol%
Total gas flow rate	200 ml/min	100 ml/min
Particle size	60-80 mesh	CaO: 16-35 mesh
Packing amount	0.2 g	ZnS: 0.2 g CaO: 0.4 g
Pressure	1 atm	1 atm

and the lines leading to the reactor were heated. The effluent gases through fixed-bed reactor were analyzed by a G.C. equipped with thermal conductivity dector (TCD) and 8 ft.×1/8 in. o.d. Chromosil 310 column operating at 50℃. The same experimental apparatus was used for the removal of SO_2 and experimental conditions were described in Table 1.

Because of difficulty of G.C. calibration for SO_2, the numeric value of SO_2 in Y-axis, Q_p, was obtained by peak area recorded and total SO_2 uptake was the product of flow rate of gas, SO_2 uptake (peak area) and time on stream.

Results and Discussion

1. Effect of Regeneration Temperature

The overall reaction consists of two consecutive gas-solid reactions as given belows:

$$ZnS(s)+3/2\ O_2(g)=ZnO(s)+SO_2(g) \quad (1)$$

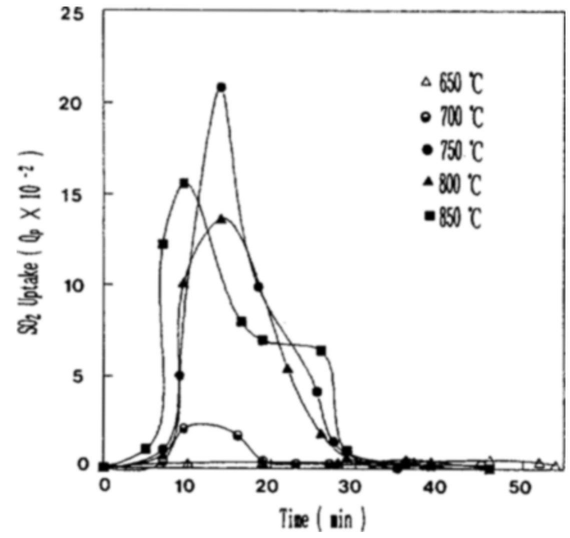

Fig. 2. Effect of temperature on the oxidative regeneration with CaO.

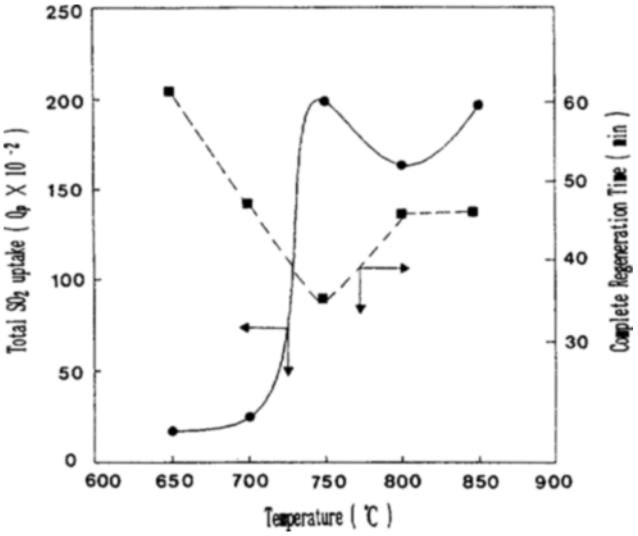

Fig. 3. Total SO_2 uptake and time needed for complete regeneration vs. temperature.

$$CaO(s)+SO_2(g)+1/2\ O_2(g)=CaSO_4(s) \quad (2)$$

The solid products of Eq. (2) are dependent of reaction temperature, composition of gaseous reactants (especially, existence of O_2) and time on stream. Below 640℃, the main product was $CaSO_3$ and gradual formation of $CaSO_4$ was occurred if the reaction time was longer [11]. It was also reported that intermediate $CaSO_3$ was formed during the conversion of CaO to $CaSO_4$ [19]. Hatfield et al. [20], from the I.R. analysis, revealed that $CaSO_3$ was the main solid product and oxidized to $CaSO_4$ near 720℃ or disproportionized to $CaSO_4$ and CaS. Furthermore CaS produced by disproportionation of $CaSO_3$ was not changed below 880℃ [21].

Fig. 2 and 3 represented the SO_2 uptake vs. reaction time and total SO_2 uptake vs. reaction temperature. For this experiment, regeneration temperature was the only variable. Oxidative regeneration of sulfided sorbent was the most active for 10 vol.% of O_2 and thin film mass transfer resistance was negligible above

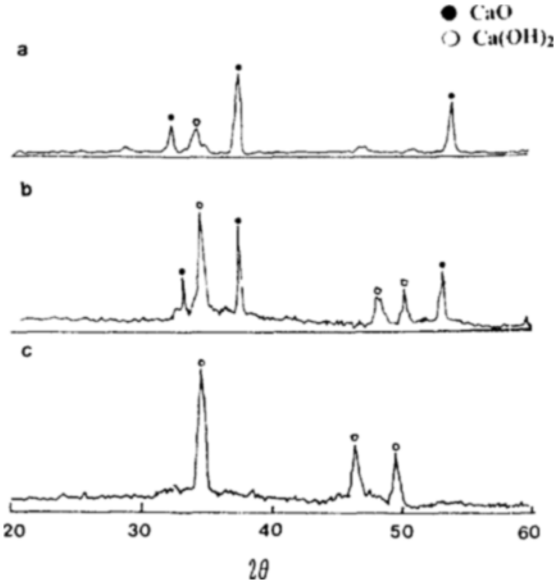

Fig. 4. XRD powder pattern for calcined CaO at 1000°C before reaction.
(A) 16-35, (B) 60-80, (C) 140-200 mesh

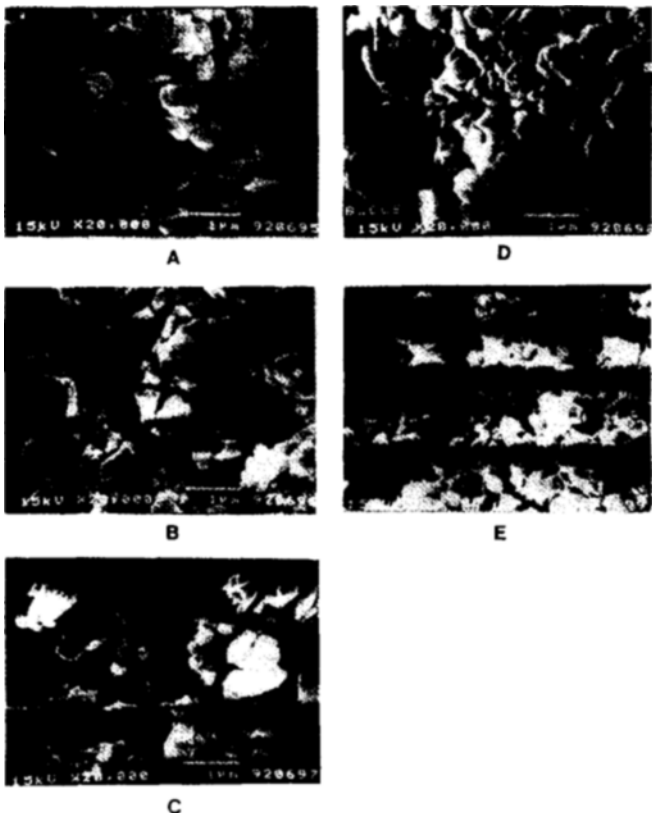

Fig. 5. SEM morphology of CaO sulfided at different temperatures.
(A) 650℃, (B) 700℃, (C) 750℃, (D) 800℃, (E) 850℃

100 ml/min (space velocity = 127 min^{-1}) of total flow rate [4]. Thus O_2 content and total flow rate were fixed as 10 vol.% and 100 ml/min, respectively. CaO sorbent for the removal of SO_2 emitted during the oxidative regeneration was 16-35 mesh and mixing ratio of CaO to sulfided sorbent was 2 : 1. Double-bed packing type was used [4]. The SO_2 uptake at 650℃ and 700℃ were little. This was considered to be caused by the fact that SO_2 generated was little during the oxidative regeneration without CaO [4] and little structural change of CaO was occurred at these temperatures [22, 23]. Furthermore SO_2 uptake at 750℃ was more than that of 800℃. This was caused by that the SO_2 generated was more at 750℃ than that of 800℃ because of vaporization of ZnS [4] and the reactivity of CaO with SO_2 was deteriorated by the structural change like sintering of CaO causing the reduction of specific surface area. It was reported that the structural change of CaO was very sensitive to temperature [23].

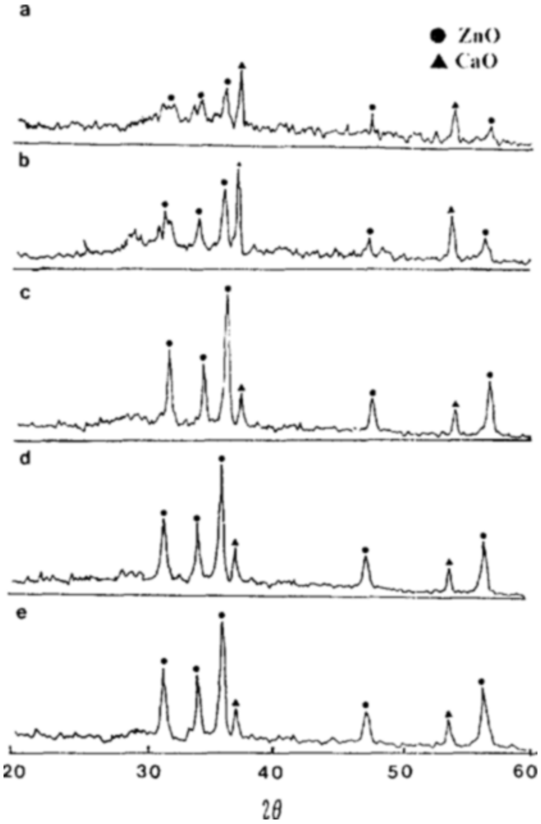

Fig. 6. XRD powder pattern for CaO (16-35 mesh) sulfided at different temperatures.
(A) 650℃, (B) 700℃, (C) 750℃, (D) 800℃, (E) 850℃

Although it was considered that CaO sorbent calcined at 1000℃ was not changed structurally due to heating only below 1000℃, slaking of CaO changed calcined CaO into poorly crystalline $Ca(OH)_2$ by absorption of H_2O even though at room temperature. This phenomenon was verified by XRD powder patterns depicted in Fig. 4 and was coincidence with the results of Dario et al. [24]. It was also reported the reactivity of CaO produced by dehydration of $Ca(OH)_2$ was better than that of pure CaO but structural change was severe at high temperture [24]. At 850℃, this structural change, which causes the reduction of specific surface area and thereby reactivity of CaO, was so severe [23-25] that the amount of emitted SO_2 was more. Moreover this structural change of CaO was accelerated in the presence of SO_2 [26].

Fig. 5 represented SEM photographes of sulfided CaO sorbents. As temperature was the higher, the agglomeration of sorbent was severe and the structural change cited previously was affirmed. XRD powder patterns of reacted CaO sorbents were depicted in

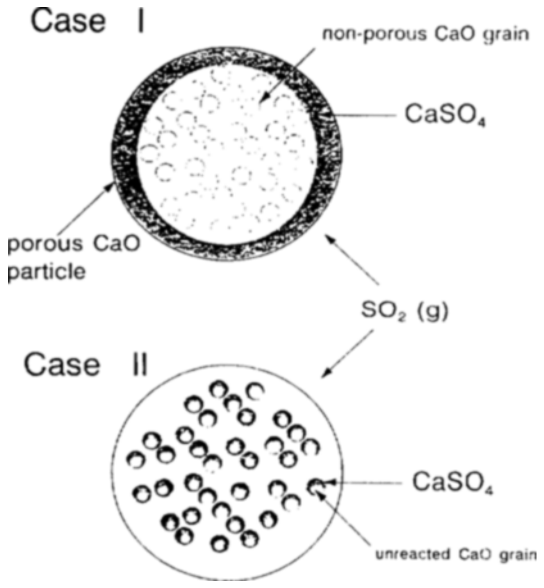

Fig. 7. Schematic diagram of CaO sulfidation model.

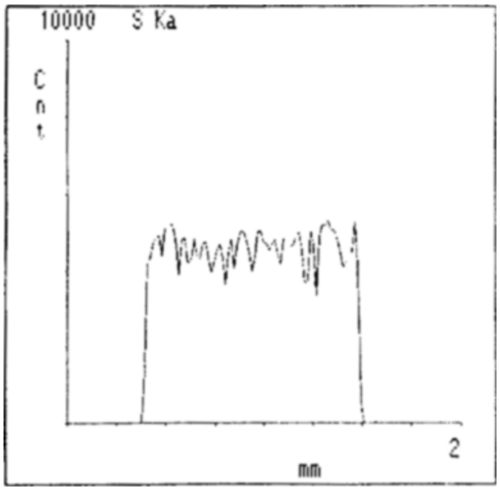

Fig. 8. EPMA sulfur profile for CaO (16-35 mesh) sulfided at 750°C.

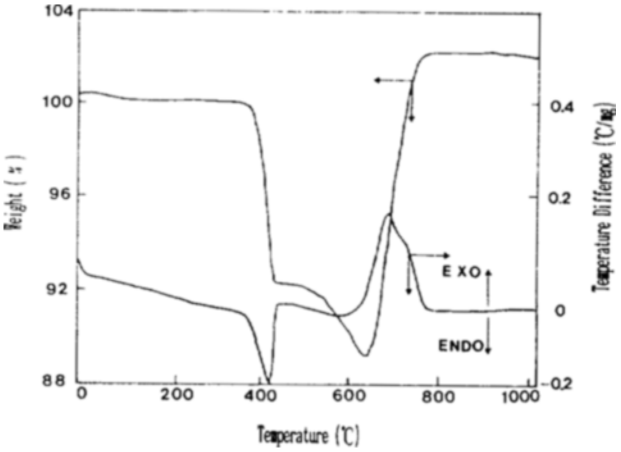

Fig. 9. DT/TGA analysis of air oxidation for sulfided sorbent mixed with CaO (16-35 mesh) calcined at 1000°C.

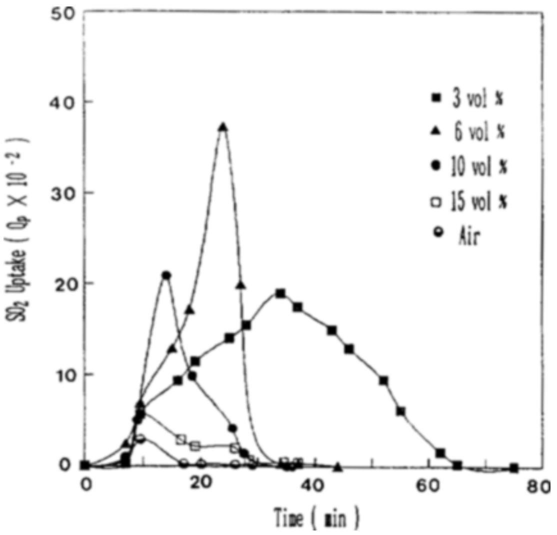

Fig. 10. Effect of oxygen on oxidative regeneration with CaO.

Fig. 6. An intriguing phenomenon was observed. From previous data, Fig. 2, the removal of SO_2 was confirmed. But XRD pattern represented not CaS and $CaSO_4$ but CaO only. On the contrary, for small particle (below 60 mesh), the complete sulfidation occurred because the reactivity is inversely proportional to particle diameter. So only $CaSO_4$ was detected by XRD analysis for sulfided sorbent at 750℃. The reaction model for this situation was supposed to be case I and case II depicted in Fig. 7. But considering the sulfur profile obtained by EPMA, Fig. 8, showing uniform spatial distribution of sulfur within particle, case II was more reasonable. Therefore diffusion through the solid product, $CaSO_4$, was considered to be rate limiting step for CaO sulfidation and this is coincidence with another's reports [27-31]. The high sensitivity of CaO-SO_2-O_2 reaction to the temperature, for example, has led some investigators to conclude that chemical reaction is rate controlling, while different features of the same data have been interpreted by others as evidence that the reaction is controlled by either diffusion of the reactive gas through the product layer formed on the CaO grains that comprise the interior of the particles [27] or combinations of diffusion and chemical reaction on the grains [28]. Especially unreacted shrinking core model was reported to be good for describing the reaction of CaO grain with SO_2 [14, 29]. Sulfidation of CaO was controlled by product-layer diffusion at the grain surface [30]. Solid product $CaSO_4$ of whch molar volume is three times as large as that of CaO, was deposited on the grain surface and plugged the pore mouth and therefore it acted as the diffusion barrier for SO_2. Among the various diffusion mechanism through the $CaSO_4$, outward growth mode representing the migration of Ca^{++} ion to $CaSO_4$ from the $CaSO_4$/CaS interface was reported to be the rate limiting step for sulfidation [31].

Fig. 9 showed TG/DGA for oxidation of sulfided sorbent mixed with 16-35 mesh CaO calcined at 1000℃ in air atmosphere. Sharp endothermic deflection near 410℃ meant dehydration of $Ca(OH)_2$, formed by slaking of CaO cited previously, and weight decrease after this was due to slow oxidation of ZnS and FeS_2 [4]. The weight increase near 610℃ represented the formation of $CaSO_4$ resulted from the reaction of CaO with SO_2 generated during the oxidative regeneration.

2. Effect of Oxygen Concentration

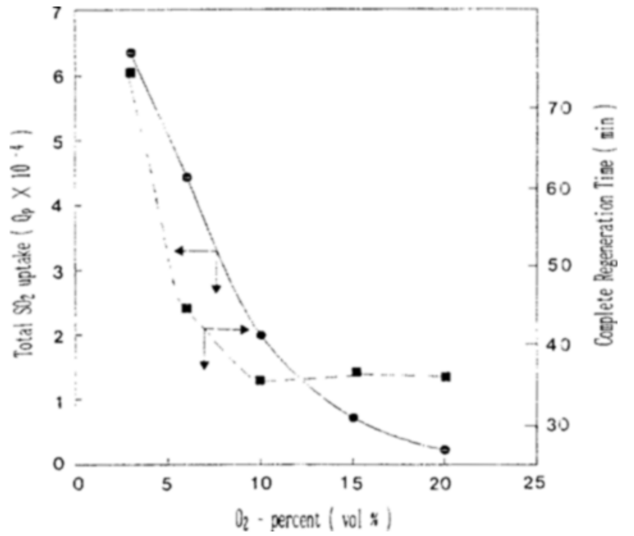

Fig. 11. Total SO_2 uptake and time needed for complete regeneration vs. oxygen content.

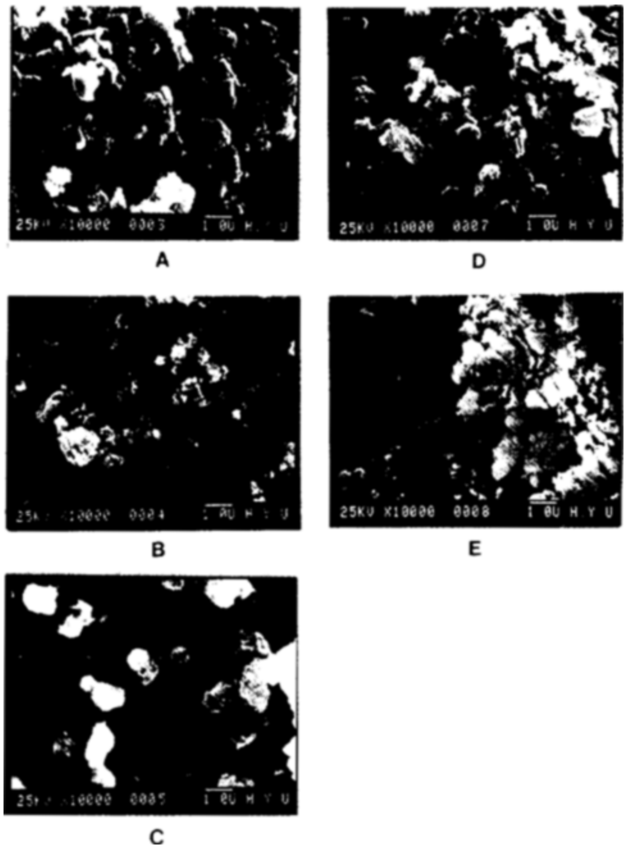

Fig. 12. SEM morphology of CaO sulfided by different oxygen content.
(A) 3 vol%, (B) 6 vol%, (C) 10 vol%, (D) 15 vol%, (E) Air

The effect of oxygen concentration was depicted in Fig. 10. In this case, O_2 concentration was the only variable and regeneration temperature was fixed at 750°C and another conditions were the same as mentioned above. One of the important results of our previous research was that total SO_2 uptake was 0.7 power with respect to O_2 till 10 vol% O_2 and decreased drastically because of temperature runaway within the reactor due to high exothermic reaction heat [4].

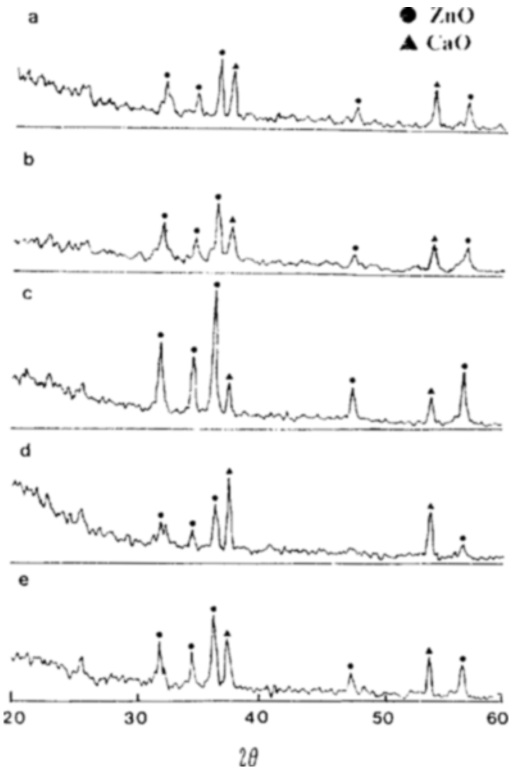

Fig. 13. XRD powder pattern for CaO (16-35) sulfided at different oxygen contents.
(A) 3 vol%, (B) 6 vol%, (C) 10 vol%, (D) 15 vol%, (E) Air

Fig. 11 depicted total SO_2 uptake vs. oxygen content. Considering the linear decrease of SO_2 till 10 vol% O_2, the reaction of CaO with SO_2 was considered to be about first order with respect to SO_2 and this was consistent with the previous researches [12, 30]. Below 6 vol% O_2, reaction time was longer and more SO_2 was emitted. This was caused by the fact that O_2 was so deficient that conversion of CaO to $CaSO_4$ occurred little and slowly [12]. Above 10 vol% of O_2, it is expected that much SO_2 was emitted because of structural change of CaO caused by temperature runaway within the reactor due to high exothermic reaction heat [4], although, the reactivity of CaO with SO_2 was accelerated by the high O_2 concentration [12] thus the SO_2 emitted was less.

SEM photographes of reacted CaO sorbent in different O_2 contents were depicted in Fig. 12. Break of surface was occurred below 6 vol% but above 15 vol%, the agglomeration of surface grains was found due to high exothermic reaction heat.

XRD powder patterns were depicted in Fig. 13. Regardless of O_2 content, ZnO and CaO were detected. The reason of detection of CaO was as same as mentioned above.

CONCLUSION

From the experimental results for oxidative regeneration of sulfided sorbent with CaO, we obtained the following conclusions.

The structural changes of CaO above 750°C deteriorated reactivity of CaO with SO_2 and resulted in increment of emission of SO_2 and that at 850°C was more severe. From the EPMA and XRD analysis, the rate limiting step for CaO sulfidation was considered to be product layer diffusion through the solid product, $CaSO_4$. The reaction of CaO with SO_2 was first order approximately and that was accelerated by high O_2 concentration.

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