

Sol–Gel Auto-Combustion Synthesis of Zinc Ferrite for Moderate Temperature Desulfurization

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Zinc ferrite as a desulfurization sorbent with an average crystallite size of about 36 nm was synthesized by a sol–gel auto-combustion method. The precursor for the sorbent was a gel obtained from metal nitrates and citric acid by a sol process. The nitrate–citrate gel exhibits a self-propagating combustion behavior, and after combustion, it can transform into a nanosized spinel structured zinc ferrite directly. The prepared sorbent has a larger specific surface area and higher reactivity when compared with the sorbent achieved by a solid mixing method, and it could efficiently reduce the H₂S concentration from 6000 ppm to less than 2 ppm at a moderate temperature range. The sulfur capacity at 400 °C reaches about 38.5 g of sulfur/100 g of sorbent, which corresponds to 96.4% of the theoretical value. The temperature programmed oxidation test for the sulfided sorbent shows that the most sulfur is desorbed before 500 °C. XRD results confirm that the sulfided sample after exposure to a 5% O₂/N₂ gas mixture at 500 °C can be regenerated completely, which indicates that the regeneration temperature of the sorbent prepared by the sol–gel auto-combustion method could be greatly reduced.

1. Introduction

The integrated gasification combined cycle (IGCC) is considered to be one of the most efficient and environmentally acceptable technologies for power generation from coal. One key part of it is the removal of pollutants from the coal-derived fuel gas. The gas produced from coal gasification contains H₂S and other hazardous sulfur compounds, which must be removed to prevent corrosion and environmental problems. Thus, the removal of H₂S in the coal gasification gas by using single- or mixed-metal oxide sorbents has been extensively investigated. Many pure metal oxides and their mixtures have been widely investigated as high-temperature desulfurization sorbents. Westmoreland et al.¹ reported a thermodynamic calculation for the feasibility study of a large number of metals on the condition that they were representative of the future high sulfur coal gasification. Several pure and mixed metal oxides, including CaO,^{2–4} ZnO,^{5–7} Fe₂O₃,⁸ ZnO–TiO₂,^{9–11} ZnO–Fe₂O₃,^{12,13}

ZnO–Al₂O₃,^{14–16} and CuO–Cr₂O₃,^{17,18} were regarded as regenerable sorbents for high-temperature desulfurization. Among these metal oxides, zinc, iron, copper, and calcium oxides have been intensively researched.

However, until now, the desulfurization processes were estimated to be practical only at high temperatures. Droog et al.¹⁹ made another suggestion recently based on the economic evaluation of IGCC that the operation at lower temperatures such as 343–538 °C could be much better than at high temperatures, as the desulfurization system components become prohibitively expensive with increasing the operation temperature but the overall IGCC process efficiency improves only a little. However, in such a low-temperature range, the reactivity of the sorbent prepared by conventional methods will be greatly decreased, which limits this procedure for practical applications. In addition, the sorbent prepared by conventional methods

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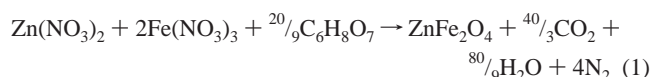
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always needs to be regenerated at high temperatures,^{20,21} which results in the sintering and loss of reactivity of the sorbent after a few cycles of sulfidation/regeneration. Recent research is centralized on improving the reactivity of the sorbent at moderate temperatures as well as reducing the regeneration temperature.

To overcome the limitations of conventional sorbent preparation techniques, the sol–gel auto-combustion method of preparing the desulfurization sorbent was explored. It is a novel method with a combination of the chemical sol–gel process and the combustion process. This method uses a solution during the initial step of the preparation process, which leads to the following advantages: (1) reactants are well-dispersed, providing a homogeneous reaction mixture; (2) reactants are in a much higher reactive state than in the corresponding solid-state reaction precursors; (3) consequently, the reaction requires less energy, and the initial reaction threshold temperature can be lowered; and (4) distribution of the components in mixed solids is more uniform and random because of the homogeneous starting mixture.^{22,23} It is for these reasons that the sol–gel auto-combustion method is widely applied for preparing ceramic and magnetic materials.^{24–26} However, adopting this method for the synthesis of a desulfurization sorbent has never been reported. The present work reports a sol–gel auto-combustion method for the preparation of a desulfurization sorbent, and zinc ferrite was chosen as the sorbent due to its superior thermodynamic properties.¹² Desulfurization behaviors of the sorbent were examined by using a fixed-bed flow-type reactor. Regeneration characteristics of the sulfided sorbent were also investigated.

2. Experimental Procedures

2.1. Sorbent Preparation. Analytical grade zinc nitrate, iron nitrate, and citric acid were used as raw materials to prepare zinc ferrite nanocomposites. The preparation process is described as follows: the molar ratio of Zn to Fe was 1:2. First, a certain amount of citric acid was weighed and dissolved in diluted water, then Zn(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O were dissolved in it with a molar ratio of total nitrates to citric acid of 1:1. A small amount of ammonia was added into the solution to adjust the pH value to about 7 and stabilized the nitrate–citrate sol. During this procedure, the solution was continuously stirred and kept at a temperature of 60 °C. Then, the stabilized nitrate–citrate sol was poured into a tray and heated slowly to 120 °C. The viscosity and color changed as the sol turned into a brown, puffy, porous dry gel. When the temperature was increased to 250 °C, the dried gel simultaneously burnt in a self-propagating combustion manner until it was completely transformed into loose powder. The as-synthesized sorbent was designated as the SG-sorbent. The overall reaction for the formation and thermal decomposition of the complex combination in this method is²⁷



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The sorbent synthesized by the solid mixing method was also prepared for a critical comparison. Detailed preparation steps are described elsewhere.²⁸ After calcination, the solid was crushed and sieved, and 124–150 μm particles were collected, which were designated as the SM-sorbent.

2.2. Characterization of Sorbents. Infrared spectra (IR) for the dried gel and SG-sorbent were recorded on a Nicolet Magna 550-II spectrophotometer from 400 to 4000 cm^{−1} by the KBr pellet method. Transmission electron microscopy (TEM) examination of the SG-sorbent was performed using a JEM 2010 electron microscope. Specific surface areas of fresh and regenerated SG-sorbent and fresh SM-sorbent were measured by the BET method using a Tristar 3000, applying adsorption isotherms of nitrogen at −196 °C. The phase identification of the fresh, sulfided, and regenerated samples was performed using an X-ray diffractometer (RAX-12) with Cu Kα radiation and operated at 20 mA and 40 kV. Average crystallite sizes can be estimated from the full-width at half-maximum (fwhm) of the strongest diffraction peak using Scherrer's formula:²⁹

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (2)$$

where D is the crystalline size, λ is the wavelength of Cu Kα, β is the fwhm, and θ is the diffraction angle of the strongest characteristic peak. Morphologies of the sorbent were observed by scanning electron microscopy (SEM).

2.3. Sulfidation and Regeneration Tests. A schematic diagram of the bench scale fixed-bed reactor system is shown in Figure 1.

Sulfidation and regeneration tests were performed in a vertical bench scale fixed-bed reactor, which was composed of quartz with an inner diameter of 1.4 cm. The reactor was placed vertically in an electric furnace equipped with a Proportional-integral-differential (PID) controller. The sorbent bed was supported with a fritted quartz disk, and the sorbents (0.3 g) were placed on the fritted quartz disk in the center of the quartz reactor. A K-type thermocouple was inserted exactly on the top of the sorbents so that the temperature could be monitored correctly. The conditions of sulfidation and regeneration and the compositions of mixed gases are presented in Table 1. Before the experiment, pure nitrogen gas (purity 99.99%) was fed into the reactor for 30 min at experimental temperatures to remove any adsorbed water and impure gaseous molecules coated on the surface of the sorbents. The concentration of H₂S was analyzed through a gas chromatograph (GC 9700) equipped with a flame photometry detector. In this paper, the sulfidation run was considered to be complete when the outlet concentration of H₂S exceeded 100 ppm and the regeneration run was performed for 1 h.

2.4. Temperature Programmed Reduction (TPR)/Temperature Programmed Oxidation (TPO) Tests. TPR was performed to study the reducibility for both SG- and SM-sorbents. A flow of 5% H₂ in N₂ was used as the reduction gas. Typically, 25 mg of dried sample was loaded into a quartz tube reactor (5 mm i.d.) and reduced by raising the temperature from 60 to 1000 °C at a temperature ramp of 10 °C/min. The effluent gas was monitored by a TCD.

TPO was performed to determine the suitable regeneration temperature for the sulfided sorbent. It was carried out by measuring the concentration of SO₂ produced by the introduction of air with a flowrate of 100 mL/min, when the ramp rate of the temperature was 10 °C/min, from room temperature to 800 °C. The SO₂ concentration was analyzed through an on-line gas chromatograph (GC 920) equipped with a flame photometry detector (FPD).

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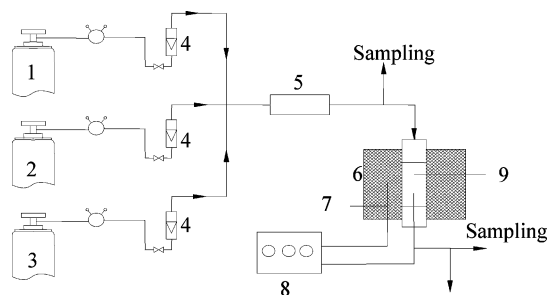


Figure 1. Schematic diagram of bench scale fixed-bed reactor system: (1) H_2 ; (2) N_2 ; (3) H_2S ; (4) flowmeter; (5) gas mixer; (6) furnace; (7) thermocouple; (8) temperature controller; and (9) reactor.

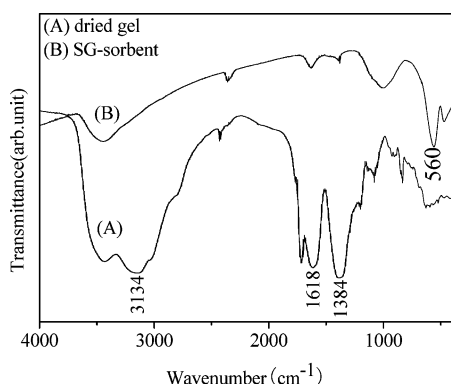


Figure 2. IR spectra of dried gel (a) and SG-sorbent (b).

Table 1. Experimental Conditions of Fixed-Bed Reactor

	sulfidation	regeneration
T ($^{\circ}C$)	350, 400, 500	500
P (MPa)	0.1	0.1
space velocity (h^{-1})	6400	6400
gas composition	H_2S : 0.6%; H_2 : 15%; N_2 : balance	O_2 : 5%; N_2 : balance

3. Results and Discussion

3.1. IR Spectra of Dried Gel and SG-Sorbent. IR spectral analysis provides evidence for the formation of zinc ferrite. It can be used to monitor the chemical and structural changes that take place during combustion and may be helpful to understand the combustion reaction mechanism. Figure 2 shows the IR spectra of the dried gel and SG-sorbent in the range of 400–4000 cm^{-1} . The dried gel showed characteristic bands at about 3134, 1620, and 1384 cm^{-1} corresponding to the O–H group, carboxyl group, and NO_3^- ion, respectively.^{30,31} The existence of the characteristic bands of NO_3^- indicates that NO_3^- as a group exists in the structure of citrate gel during the gelation of the mixed solution formed from nitrates and citric acid. In the IR curves of the SG-sorbent, there is only one significant spectroscopic band at about 560 cm^{-1} . It is the characteristic band of zinc ferrite, which indicates that the ferrite is directly formed after combustion. This can also be proven by XRD results. As seen in Figure 3a, the principal peak represents zinc ferrite according to the Joint Committee on Powder Diffraction System (JCPDS).³² The disappearance of the characteristic bands of the carboxyl group and NO_3^- ion in the IR spectrum curve of the SG-sorbent reveals that the carboxyl group and NO_3^-

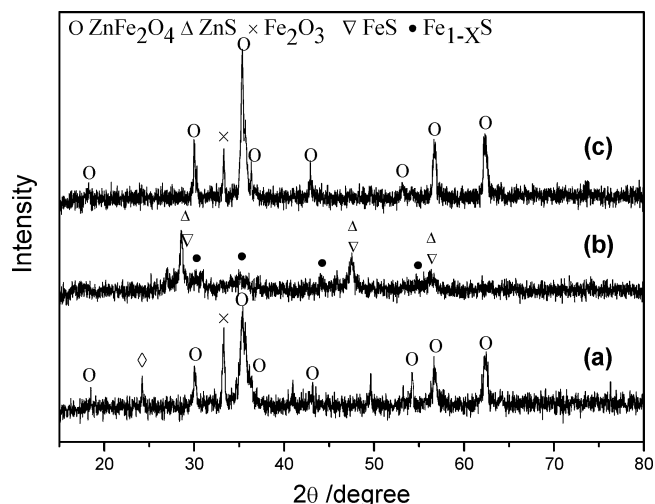


Figure 3. XRD patterns of SG-sorbents before and after sulfidation and after regeneration: (a) fresh; (b) after sulfidation; and (c) after regeneration.

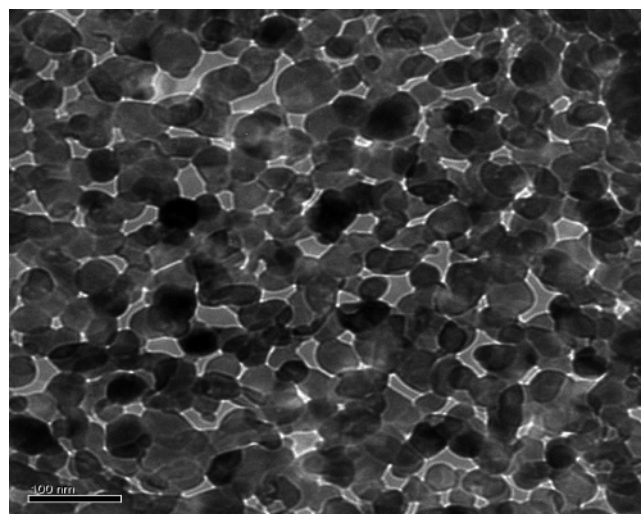


Figure 4. TEM photograph of SG-sorbents.

Table 2. Physical Properties of Fresh and Regenerated SG-Sorbents and Fresh SM-Sorbent

sorbent	BET surface area (m^2/g)	pore volume (cm^3/g)	av pore diameter (nm)	av crystallite size (nm)
SG-fresh	25.0	0.082	21.8	36.2
SG-regenerated	17.3	0.051	33.8	45.3
SM-fresh	1.7	0.009	21.8	605.4 ^a

^a Calculated from BET area.

ion take part in the reaction during combustion. Therefore, the combustion can be considered to be a heat-induced exothermic oxidation–reduction reaction where nitrate ions act as oxidizers and the carboxyl group acts as a reducing agent. Owing to the exothermic characteristic of the reaction, high temperatures ensure the crystallization and formation of oxides in a short amount of time.

As compared to the solid mixing method for synthesizing zinc ferrite at about 1180 $^{\circ}C$,²⁸ the sol–gel auto-combustion method could be operated at a much lower temperature, which could reduce the energy consumption and prevent the sorbent from sintering. As a result, the sorbent prepared by this method has a larger specific surface area, as shown in Table 2.

The TEM photograph of the SG-sorbent, shown in Figure 4, indicates that the powders are nanocrystalline with their sizes

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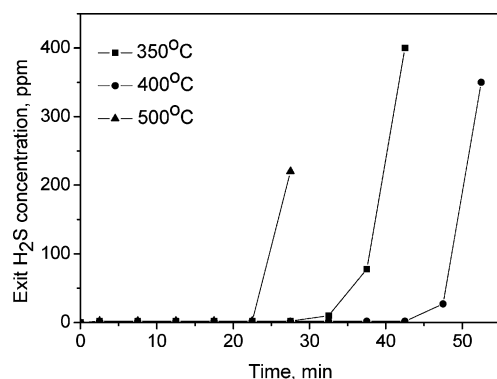


Figure 5. H₂S breakthrough curves of SG-sorbent at various sulfidation temperatures.

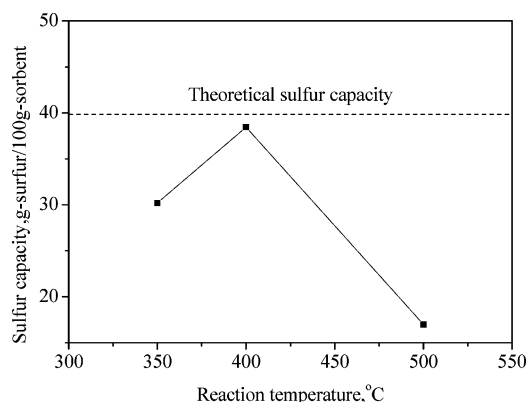


Figure 6. Sulfur capacity as a function of reaction temperature.

ranging between 30 and 40 nm, as measured using the XRD method. This reveals that the SG-sorbent is well-dispersed and that no aggregates are formed during combustion.

3.2. Sulfidation and Regeneration Tests. *3.2.1. Sulfidation.* The SG-sorbent was tested at three different reaction temperatures of 350, 400, and 500 °C, respectively, to examine their reactivity. The breakthrough curves of the reaction temperature on the SG-sorbent are presented in Figure 5. As can be seen from Figure 5, the SG-sorbent could efficiently reduce the H₂S concentration to less than 2 ppm for all reaction temperatures prior to the breakthrough.

The overall sulfur capacity of different reaction temperatures is calculated from the result of Figure 5. The sulfur capacity is expressed as grams of sulfur per 100 grams of sorbent, and the results are shown in Figure 6. The sulfur capacity is calculated according to the following experimental expression:

$$\text{g of sulfur/100 g of sorbent} = \frac{F_s}{B_T} W \quad (3)$$

where F_s represents as mass flow rate of sulfur (g/min), B_T represents the breakthrough time, and W indicates the weight of packed fresh sorbent. The theoretical sulfur capacity of zinc ferrite is approximate 39.9 g of sulfur/100 g of sorbent, which is roughly calculated based on the postulation that the final products are ZnS and FeS. It is interesting to note that as the temperature increased, the sulfur capacity exhibited a different change style. When the temperature increased from 350 to 400 °C, the sulfur capacity increased with an increasing temperature. However, the sulfur capacity decreased greatly with an increasing temperature to 500 °C. At 400 °C, the sulfur capacity reached about 38.5 g of sulfur/100 g of sorbent, nearly approaching the theoretical value. This result seems reasonable

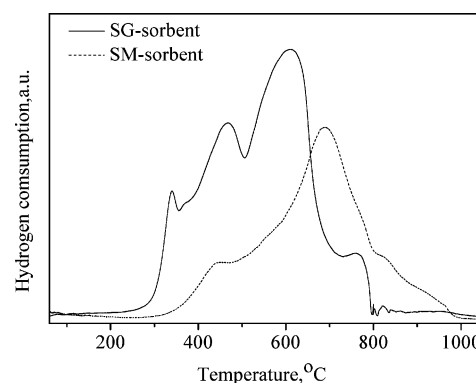
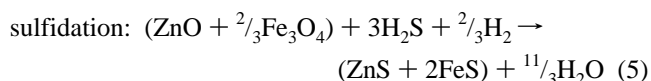
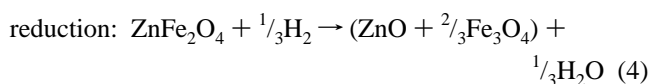


Figure 7. H₂-TPR profiles of SG- and SM-sorbents.

to suggest that the sol–gel auto-combustion method would be a potential approach for the synthesis of the desulfurization sorbent, as the sulfur capacity as high as the theoretical value has rarely been reported in the literature.^{33,34} It is for this reason that in the present work the reaction temperature of 400 °C was chosen for the sequence of experiments for this study.

The inferior desulfurization performance of the SG-sorbent operated at 500 °C could be explained according to the conclusions obtained by Focht et al.^{34,35} They found that in the temperature range of 500–700 °C, the reducing atmosphere of coal gas causes the zinc ferrite to separate into the component oxides (ZnO and Fe₂O₃) and causes further reduction of Fe₂O₃ to Fe₃O₄ at above 600 °C. Therefore, the primary reactions at temperatures above 500 °C suggested by Focht et al.^{34,35} are



However, the sorbent they studied was prepared by the solid mixing method. As mentioned previously, the sorbent prepared by the sol–gel auto-combustion method has a larger specific surface area, which logically affects positively the overall reaction rate, leading to a higher reactivity so that reactions 4 and 5 can proceed at relatively low temperatures. This could be confirmed by the TPR results, which are shown in Figure 7.

As can be seen from the figure, two kinds of reduction behaviors are observed. The SG-sorbent shows a TPR trace characterized by four poorly resolved reduction peaks in the temperature range of 300–800 °C. These peaks reflect the reduction of the oxygen species in the main crystalline phases of the solid and can be ascribed to the reduction of zinc oxide and iron oxide. For that in the presence of H₂, zinc ferrite is decomposed into ZnO and Fe₂O₃, and Fe₂O₃ is further reduced to metallic iron.³⁶ The reduction profile of Fe₂O₃ has been reported to present two peaks, corresponding to the reduction process of Fe₂O₃ to Fe₃O₄ and Fe₃O₄ to Fe.³⁷ In contrast, the TPR profile of the SM-sorbent shows a relatively simple trace

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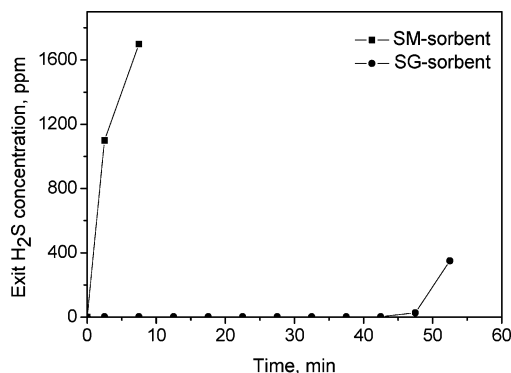
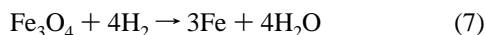
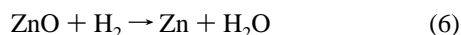


Figure 8. H₂S breakthrough curves for SG- and SM-sorbents at 400 °C.

with peaks appearing in the range of 400–950 °C. It is interesting to note that most peaks of the SG-sorbent appeared in advance of those of the SM-sorbent, which indicates that the reducibility of the sorbent prepared by the sol–gel auto-combustion method is greatly improved and that the reduction of it could occur at lower temperatures. When the temperature is increased, the following two reactions would compete with reaction 5:



Reactions 6 and 7 become so drastic that metal oxides are excessively reduced to metallic zinc and iron as the temperature is further increased. It is well-known that elemental zinc could be vaporized easily at high temperatures and that the sulfidation kinetics of metallic iron with H₂S is much lower than the corresponding oxides. The aforementioned negative effects would all be responsible for the lower efficiency of the SG-sorbent at high temperatures.

After the sulfidation experiment at 400 °C, the XRD results of the sulfided sample (Figure 3b) show diffraction peaks shifted to lower 2θ angles as compared to the fresh sorbent, which indicates that the metal oxides in the fresh sorbent are converted into metal sulfide. These peaks are identified as ZnS and FeS according to JCPDS files. Besides ZnS and FeS, poor crystalline phases are also found for Fe_{1-x}S.

To compare the desulfurization behaviors of sorbents prepared by different methods intuitively, the sulfidation experiments for both SG-sorbent and SM-sorbent at 400 °C were carried out. The breakthrough curves of the synthesizing method on zinc ferrite are present in Figure 8. It is quite evident from the figure that the SG-sorbent showed an excellent desulfurization performance while the SM-sorbent nearly has no reactivity under this temperature. This fact indicates that the desulfurization behaviors of the SG-sorbent are different from those of the SM-sorbent. This can be ascribed to the difference of physical and chemical properties of sorbents prepared by different methods. The sorbent prepared by the sol–gel auto-combustion method has a larger specific surface area, which exposes an increased number of adsorption sites for H₂S per gram of solid, leading to a higher absorption rate. In addition, as is known, there are small dimensions of nanocrystals, and an important fraction of the atoms is on the surface, which induces properties that are different from a polycrystalline sorbent obtained through the solid mixing method. This can be confirmed by TPR results.

3.2.2. Regeneration. Commercial interest in any sorbent will be determined not only on the basis of its behavior during

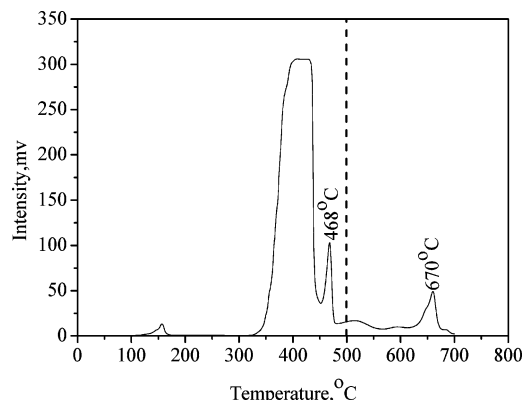


Figure 9. TPO profile of the sulfided SG-sorbent.

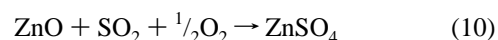
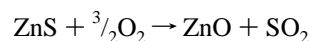
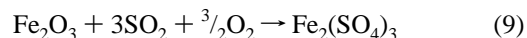
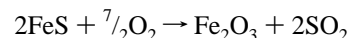
sulfidation but also upon its regeneration characteristics and durability through a number of sulfidation/regeneration cycles. The regeneration characteristics of a sorbent are very important for its application in industry. The main problems of the regeneration process of most desulfurization sorbent systems are associated with the regeneration at high temperatures,^{20,21} which could lead to the sintering and loss of reactivity of the sorbent. More attention should be paid on how to reduce the regeneration temperatures.

To determine the suitable regeneration temperature of the SG-sorbent after sulfidation, the TPO for the sulfided sample was carried out. The TPO profile of the sulfided sample is illustrated in Figure 9.

It can be noted from the figure that the most sulfur was released within the temperature range of 350–450 °C. The main reaction occurring in this temperature range is



Before 500 °C, it seems that the sulfided sample almost regenerates completely. The small peaks at about 468 and 670 °C may be due to the decomposition of Fe₂(SO₄)₃ and ZnSO₄, respectively. As reported by Krishnan et al.,³⁸ zinc and iron sulfate form during regeneration at low temperatures and high SO₂ and O₂ partial pressures according to the following mechanisms:



Sulfate formation according to reactions 9 and 10 can be significant, depending on gas composition, at temperatures below the thermal decomposition temperatures of Fe₂(SO₄)₃ and ZnSO₄. To prevent sulfate formation, Cook et al.³⁹ suggested exposing the sorbent to temperatures above the thermal decom-

(38) Krishnan, G. N.; Tong, G. T.; Lamoreaux, R. H.; Brittain, R. D.; Wood, B. J. In *A Study of Sulfate Formation during Regeneration of Zinc Ferrite Sorbents*, Proceedings of the 5th Annual Contractor's Meeting on Contaminant Control in Coal-Derived Gas Streams, U.S. Department of Energy/METC, Morgantown, WV, 1985; pp 6–18.

(39) Cook, C. S.; Gal, E.; Furman, A. H.; Ayala, R. E. In *Integrated Operation of a Pressurized Fixed-Bed Gasifier and Hot Gas Desulfurization System*, Proceedings of the 8th Annual Gasification and Gas Stream Cleanup Systems Contractor's Meeting, U.S. Department of Energy/METC, Morgantown, WV, 1988; pp 11–20.

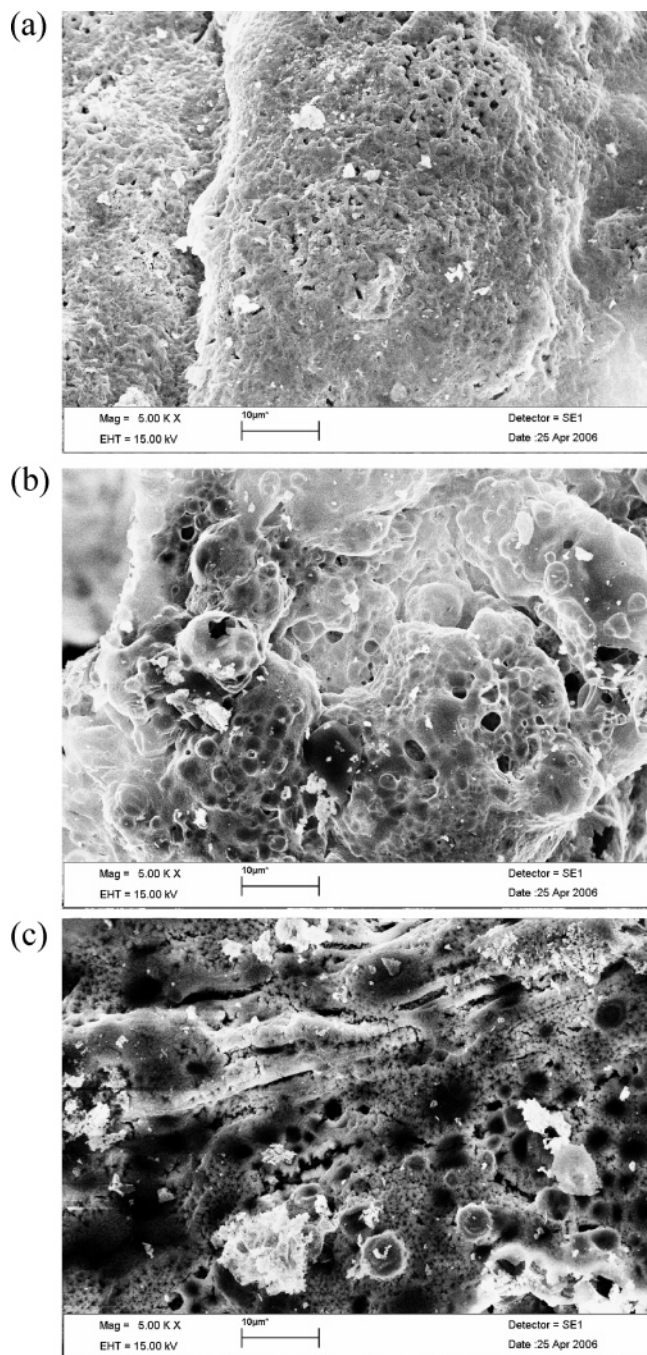


Figure 10. SEM morphologies of SG-sorbents: (a) fresh; (b) after sulfidation; and (c) after regeneration.

position of iron and zinc sulfate at the end of regeneration. However, the negative effects resulting from sulfate formation could not be avoided. Therefore, a low O_2 partial pressure was applied in the present work, and the regeneration experiment was repeated in a fixed-bed reactor at 500 °C for 1 h. XRD results (Figure 3c) show that it can be regenerated completely under this temperature. There are no other crystalline phases in the regenerated sorbent except for a small amount of Fe_2O_3 ,

which indicates that the sorbent prepared by the sol–gel auto-combustion method could be regenerated even at 500 °C. This value is much lower than the minimum temperatures required to regenerate as reported by others.^{20,21}

After regeneration, the physical properties of the sorbent have changed, as can be seen in Table 2. The reasons for this deterioration are not clear. However, the fact that the structure and pores of the sorbents were broken during the sulfidation and regeneration process should be considered seriously. This can be confirmed by SEM analysis. Figure 10 shows SEM morphologies of the fresh, sulfided, and regenerated SG-sorbent. These photographs demonstrate a drastic change in the texture and morphology of the sorbent after sulfidation and regeneration. There are many pores in the fresh sorbent, in agreement with its relatively high BET value (Table 2). After sulfidation and regeneration, the pores become larger, which is in harmony with the relative decrease in the BET area and increase in the pore diameter of the sorbent (Table 2). These could be ascribed to the spallation or cracking caused by the expansion/contraction of the sorbent during sulfidation and regeneration. That is to say, volume expansion generally occurred during the sulfidation process as the metal oxide was converted into the metal sulfide while contraction occurred during the regeneration process as the sorbent returned to its original oxide phase. For example, as calculated by Jun et al.,⁴⁰ when ZnO (molar volume: 14.34 mL/mol) was converted into ZnS (molar volume: 23.85 mL/mol), the percent of its molar volume expansion was 66.2%. The same degree of volume contraction occurs during the regeneration process. As a result, the volume expansion/contraction of zinc ferrite is sufficient for the sorbent to be broken.

4. Conclusion

The following conclusions can be derived from the results of the present work: (1) the sol–gel auto-combustion method is a novel and simple way to prepare desulfurization sorbents. The fine nanocomposites of zinc ferrite can be formed directly via combustion of the gel, without further calcination at high temperatures. (2) The SG-sorbent has a much larger specific surface area and higher reactivity, which result in the low outlet concentration of H_2S and a high sulfur capacity. (3) TPR results show that the SG-sorbent is reduced more easily, which limits it for being used at high temperatures. (4) According to the TPO result, the SG-sorbent could be regenerated completely at 500 °C, which is much lower than the values reported by others. (5) The physical properties of the regenerated sorbent have changed in some way as compared to the fresh sorbent. The volume expansion/contraction during sulfidation and regeneration should be considered to be one of the main reasons.

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(40) Jun, H. K.; Lee, T. J.; Ryu, S. O.; Kim, J. C. *Ind. Eng. Chem. Res.* **2001**, *40*, 3547–3556.