

High temperature removal of hydrogen sulfide using an N-150 sorbent

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Abstract

In this study, an N-150 sorbent was used as a high temperature desulfurization sorbent for the removal of hydrogen sulfide from coal gas in a fixed bed reactor. The results indicate that the N-150 sorbent could be used for H₂S removal in the tested temperature ranges. Regeneration test also reveals that utilization of the N-150 sorbent maintains up to 85% compared to the fresh sorbent. No significant degeneration occurs on the N-150 sorbent. In addition, various concentrations of H₂S, H₂ and CO were also considered in the performance test of the N-150 sorbent. Except for H₂S, H₂ and CO act the important roles in the high temperature desulfurization. By increasing the H₂ concentration, the sulfur capacity of the sorbent decreases and an adverse result is observed in the case of increasing CO concentration. This can be explained via water-shift reaction. On the basis of the instrument analysis, X-ray powder diffraction determination and SEM images with EDS spectrum characterization, residual sulfur is found in the regenerated N-150 sorbent and this sulfur species is sulfate which resulted by incomplete regeneration. The sulfate formation and sintering effect are major reasons to cause activity loss in the sulfidation/regeneration cycles.

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Keywords: N-150 sorbent; High temperature desulfurization; Hydrogen sulfide; Residual sulfur; Sulfate

1. Introduction

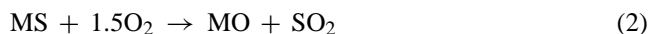
In recent year it has been widely recognized that advanced electric power generation system such as integrated gasification combined cycle (IGCC) and molten carbonate fuel cells (MCFC) are clean electric power generation technology. These emerging technologies not only improve the higher thermal efficiency but also eliminate negative environment impacts compared to conventional coal combustion. In IGCC system, coal is gasified with a stream under high temperature, which produces an abundance of CO and H₂, which are the main species for electric power generation. Generally, sulfur exists naturally in coal. However, during coal gasification the sulfur is often transferred into hydrogen sulfide and small amounts of other sulfur-containing compounds. Hydrogen sulfide is a toxic and malodorous gas as well as is the sources of the acid rain when oxidized to sulfur oxide. Thus, it is nec-

essary to remove in order to avoid corrosion of gas turbine and related equipment.

High temperature desulfurization technique has received a great deal of attention because this method can reduce H₂S down to 10 ppm as well as prevent heat loss [1,2]. The basic high temperature desulfurization reaction scheme may be represented as follows:



where MO and MS are the metal oxide and metal sulfide, respectively. The sulfide sorbent also can be regenerated through reaction with diluted air:



N-150, is a commercial catalyst of NISSAN GIRDLER, which consist of 30% MnO_x and 60% Fe₂O₃ and 10% inert material. This product was widely employed as an environmental catalyst for incinerating VOCs and sulfur-containing VOCs in the early study of our group [3–5]. In the 1970s, Westmoreland et al. screened 28 solid metal

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Table 1
The basic properties of the N-150 sorbent

Shape	Bulk density (g/cm ³)	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
Cylinder	2.2	129.1	0.23	69.8

oxides as high temperature desulfurization sorbents and evaluated their potential via thermodynamic considerations. Of all the candidate solid metal oxides, both manganese and iron oxides showed the thermodynamic feasibility for high temperature desulfurization [6]. Since N-150 mostly contains a large number of active species, this product can be used as a high temperature desulfurization sorbent. Therefore, the main objective of this study was to employ and characterize the feasibility and potential of N-150. Characterization of N-150 was also identified by X-ray powder diffraction (XRPD), and scanning electron microscopy/energy dispersion spectroscopy (SEM/EDS).

2. Materials and methods

N-150 sorbent supplied by the NISSAN GIRDLER Company, Japan, was used in this study. Its basic properties are given in Table 1. A schematic diagram of the lab-scale experimental system is shown in Fig. 1. Briefly, the sulfidation experiment mainly consisted of three sections: (1) a coal gasi-

fied gas simulation system; (2) a reactor system; and (3) an effluent analyzing system. The composition of major simulation coal gases were composed of 1% H₂S, 30% CO, 20% H₂, and 49% N₂, which were similar to the quenched exit gas of the popular KRW coal gasifier at 810 K [7]. Gases were supplied from gas cylinders and flow rates were monitored through mass flow controllers. Prior to entering the reactor the gases were conducted into a mixing pipe to confirm that mixture gases were in turbulence.

The desulfurization was performed in a vertical bench-scale fixed bed reactor, which made of quartz and having an i.d. of 1.6 cm. The reactor was placed vertically in an electric furnace equipped with PID controller. The sorbent bed was supported with a fritted quartz disk, and the sorbent was 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 sorbent so that the temperature could be monitored correctly. The sorbent sample was placed in the center of the reactor at the packed height of 0.5 cm. Before the sulfidation proceeding, a pure nitrogen gas (purity 99.99%) was fed into the reactor for 30 min at 773 K to remove any adsorbed water and impure materials coated on the surface of the sorbent. In addition, a blank breakthrough experiment also was executed under the same condition to verify that no reaction was taking place between H₂S and lines/reactor anywhere.

The inlet and outlet concentration of H₂S was analyzed through an on-line gas chromatograph (Shimadzu, GC-14B) equipped with a flame photometry detector (FPD) and fit-

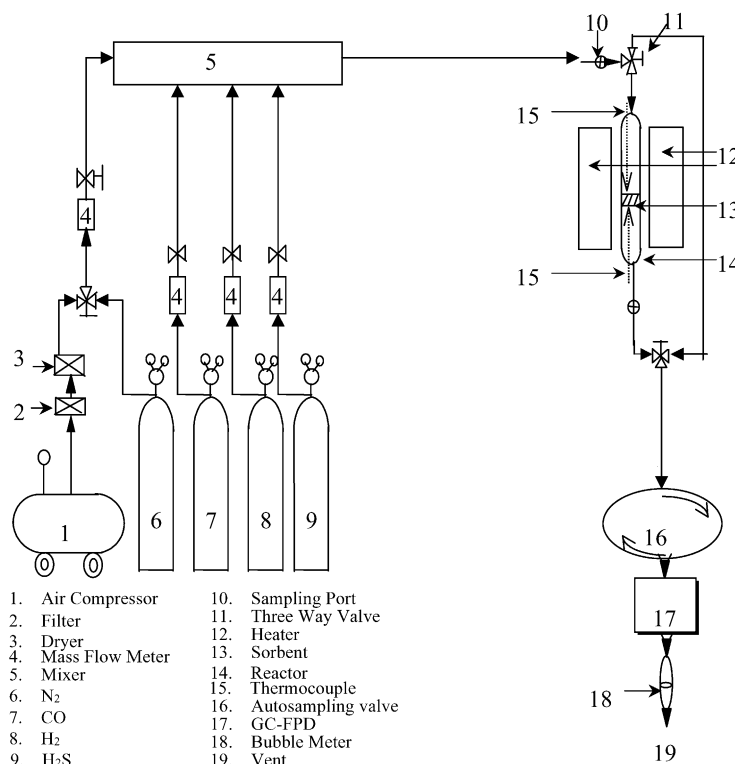


Fig. 1. A schematic diagram of the lab-scale experimental system.

ted with a GS-Q capillary column. A six-port sampling with 0.5 mL sampling loop was used to sample the inlet and outlet concentration of H₂S. The inlet and outlet gas stream was sampled every 3 min in all cases.

The overall experiment consisted of a sequence sulfidation and regeneration runs. The sulfidation run was conducted at 773 K with 1% H₂S mixture gas and the space velocity was controlled at 14,500 h⁻¹. This run was considered complete when a breakthrough point appeared. Here, a “breakthrough point” was defined as the time of the abrupt change of the H₂S concentration in exit gas. Following the sulfidation run, the reactor was purged with nitrogen gas for 15 min, and then regeneration was begun at 773 K with 5% O₂ under the same space velocity, 14,500 h⁻¹. The regeneration was terminated when the SO₂ concentration of the effluent gas was below 50 ppm.

Crystalline structures of fresh, sulfided and regenerated N-150 sorbent were determined by X-ray powder diffraction (RIGAKU Model D/MAX III-V) with a Cu K α radiation. The applied current and voltage were 30 mA and 40 kV, respectively. The diffraction patterns were recorded from 3 to 90° with a scan rate of 3°/min. Morphological of N-150 sorbent was observed by scanning electron microscopy/energy dispersion spectroscopy (Philips XL40 FE-SEM).

3. Results and discussion

Initially, N-150 sorbent was performed at three different reaction temperatures 673, 773, and 873 K, respectively. The purpose of this test was to examine the reactivity of N-150 sorbent. The breakthrough curves of reaction temperature on N-150 sorbent are present in Fig. 2, which shows that N-150 sorbent can reduce the concentration of H₂S below to 10 ppm for all reaction temperatures prior to breakthrough. The breakthrough points for 673, 773, and 873 K are 77, 81,

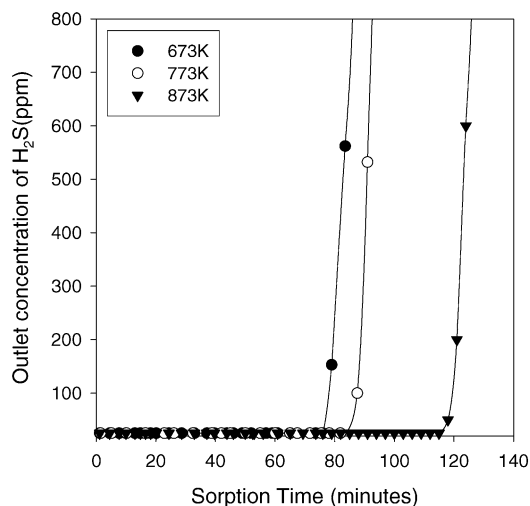


Fig. 2. The breakthrough curves in sulfidation tests with N-150 sorbent at 673, 773, and 873 K (1% H₂S; CO 30%; H₂ 20%; with balance N₂).

and 120 min, respectively. The overall sulfur capacity of the different reaction temperatures are calculated from the result of Fig. 2. The sulfur capacity is expressed as “g-sulfur/100 g-sorbent” and the result is shown in Fig. 3. The sulfur capacity is calculated according to following experimental expression:

$$\text{g-sulfur/100 g-sorbent} = \frac{F_s \times B_T}{W_i} \quad (3)$$

In this expression F_s represents as mass flow rate of sulfur, g/min. B_T represents as the breakthrough time, and W_i indicates a weight of packed N-150 sorbent. On the other hand, the theoretical sulfur capacity could be roughly calculated based on 30% Mn₂O₃ and 60% Fe₂O₃ with final products MnS and FeS, respectively. According to the known H₂S concentration, flow rate and sorbent loading weight, the theoretical sulfur capacity was determined about 38 g-sulfur/100 g-sorbent. It is clearly shown that both breakthrough time and sulfur capacity are increased with reaction temperature. Reaction temperature up to 873 K, the N-150 sorbent exhibits the highest sulfur capacity with a 37.76 g-sulfur/100 g-sorbent. This value is approaching to the theoretical sulfur capacity. This result seems reasonable to note that reaction temperature of 873 K is the optimal condition in this study due to its best sulfur capacity compared to other reaction temperatures for the N-150 sorbent. In fact, the suitable reaction temperature of the sorbent reactor in commercial pilot-scale gasifier plants has been estimated to be in the moderate temperature range of 623–823 K [7–9]. Some amount of alkali compounds in coal evolves as a gas phase and the vaporized alkali compounds contained in the coal gas are of great concern. When the coal gas with alkali vapor is introduced into a gas turbine, the alkali vapor cause corrosion of the surface of turbine blades especially at a high temperature [10,11]. To overcome this problem it is necessary to decrease temperature and to further prevent this phenomenon taking place. Recent researches also point out that increasing operating tempera-

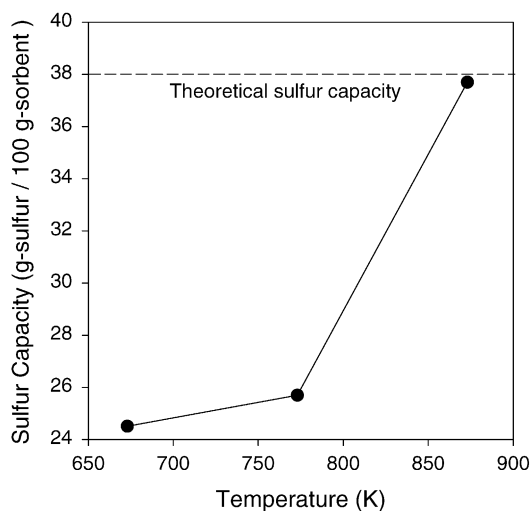


Fig. 3. Sulfur capacity as a function of the reaction temperatures.

ture leads to desulfurization system components to be prohibitively expensive. Overall efficiency of the IGCC process obtainment of carrying out desulfurization above 823 K may not be sufficient to justify operation at such high temperature. The optimum desulfurization temperature appears to be in the temperature range of 623–823 K, where technical viability and process efficiency result in a lower overall process cost [8,12]. In this work, reaction temperature of 773 K was chosen to carry out the experiments for the sequence of this study.

The results of two sulfidation/regeneration cycles on the N-150 sorbent are presented in Fig. 4. As can be seen in this figure the N-150 sorbent does not appear to have degeneration. A slight deactivation is observed after the first regeneration. Fresh N-150 sorbent achieves an effective sulfur capacity for its capture approximating about 26 g-sulfur/100 g-sorbent. This value corresponds to about 68% utilization compared to the theoretical sulfur capacity. After the first and second regeneration the breakthrough times for the first and second cycle are approximately 76 and 78 min, respectively. The sulfur capacity of the regenerated sorbents remains about 85% utilization compared to the fresh sorbent. These imply that N-150 sorbent maintains its efficiency for H₂S removal.

In the coal gasification process, H₂S concentration depended upon the type of coal and gasification condition. In general, the concentration of H₂S varied from thousands ppm to a percentage level. An experiment with N-150 sorbent containing a different concentration of H₂S but identical CO and H₂ concentrations was carried out at the temperature of 773 K. Fig. 5 shows the sulfur capacity as a function of inlet concentration of H₂S. As shown, lowering H₂S concentration increases slightly sulfur capacity. This is because that higher H₂S concentration resulted in faster formation of metal sulfide (FeS and MnS). Metal sulfides are dense materials, which

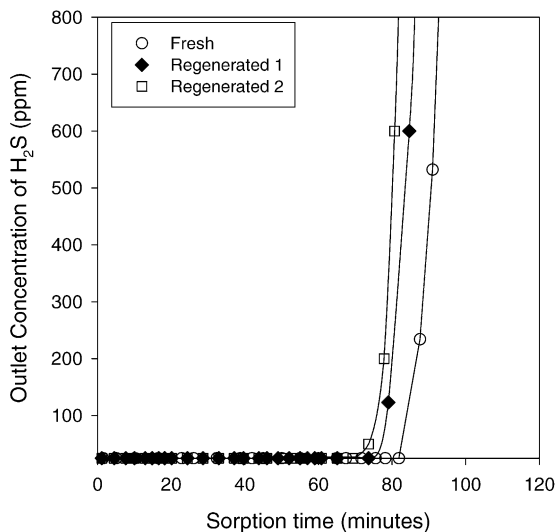


Fig. 4. H₂S breakthrough curves for N-150 sorbent in twice sulfidation/regeneration cycles.

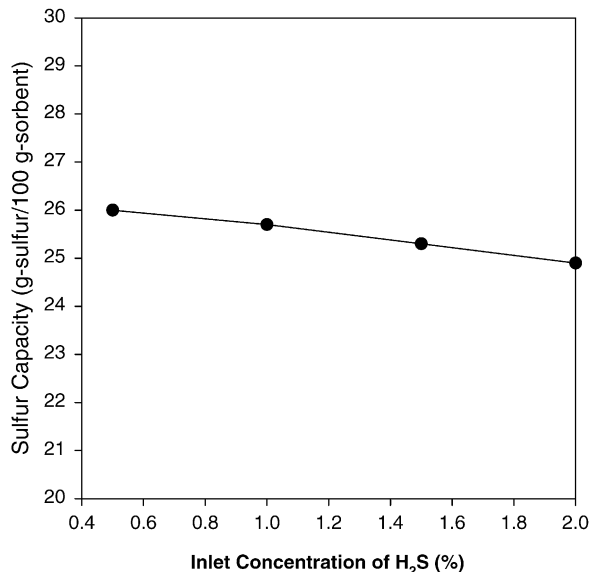


Fig. 5. Sulfur capacity variation as a function of the inlet H₂S concentration at 773 K (CO 30%; H₂ 20%; with balance N₂).

will increase mass transfer resistance and repress further H₂S diffusion into the core of sorbent. Nevertheless, sulfur capacity varied from 26.2 to 25.3 g-sulfur/100 g-sorbent in H₂S concentration ranges from 0.5 to 2%. There was no huge change in H₂S concentration, which implies that N-150 sorbent could be applied in hot coal gas desulfurization.

In addition to H₂S, CO and H₂ are principal products from coal gasification process. Unlike H₂S, CO and H₂ are called as syngas, which are the main shaft in the electric power generation. They act dissimilar roles in desulfurization stage. Figs. 6 and 7 exhibit sulfur capacity behavior with varied concentration of H₂ and CO, respectively. It is suddenly observed that CO presence is a positive effect, while H₂ appears

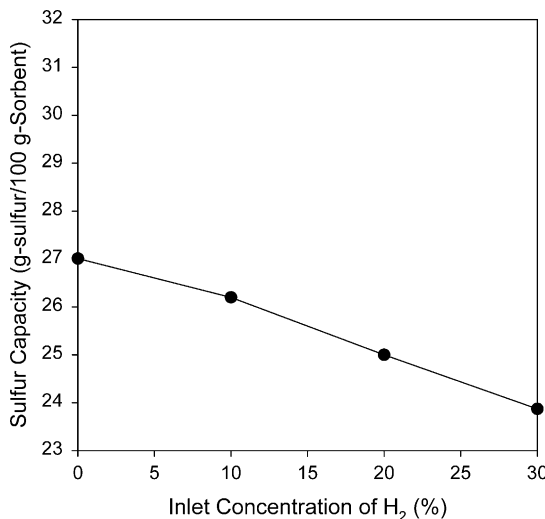


Fig. 6. Sulfur capacity variation as a function of the inlet H₂ concentration at 773 K (CO 30%; H₂S 1%; with balance N₂).

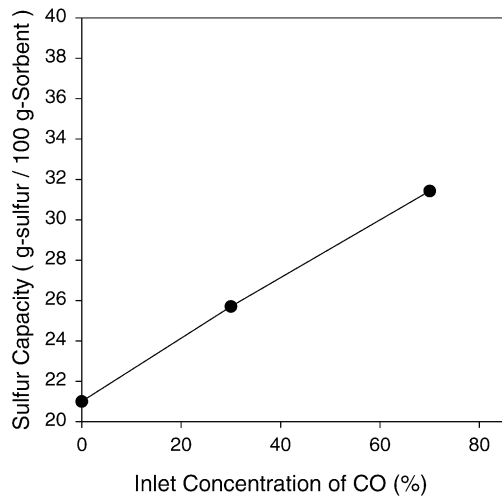
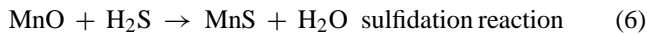


Fig. 7. Sulfur capacity variation as a function of the inlet CO concentration at 773 K (H₂ 20%; H₂S 1%; with balance N₂).

a negative effect. Furthermore, these figures also show that the magnitude of sulfur capacity is more extent for CO. Although CO and H₂ are reduction gases, however, their influence behavior is contrary.

This positive and negative effect can be explained by the water-shift reaction and sulfidation reaction:



The water-shift reaction favors toward right side according to LeChatelier’s principle when CO concentration increasing. This also means that H₂O is consumed via water-shift reaction. Lower H₂O content will favor the sulfidation reaction; therefore, increasing carbon monoxide concentration will enhance the desulfurization progress. On the other hand, increasing concentration of H₂, the reaction favors toward left side for water-shift reaction and results in formation of H₂O. Similarly, sulfidation progress is inhibited due to excess H₂O formation from water-shift reaction in sulfidation reaction.

X-ray powder diffraction analysis of fresh, sulfided and regenerated N-150 sorbents are present in Fig. 8. For fresh N-150 sorbent one intense peak is observed around 2θ = 26.62°. According to the Joint Committee on Powder Diffraction System (JCPDS) file [13], the principal peak represents MnOOH and this material appears as a strong crystalline structure. In addition to the intense manganese oxide peak, major active species present in N-150 sorbent are iron oxides. Only poor crystalline phase are detected at 2θ = 40.97 and 54.51° for α-Fe₂O₃. The absence of intense XRPD peaks in iron oxide may be indicated that iron oxides are present in a highly dispersed amorphous state. Besides iron oxides,

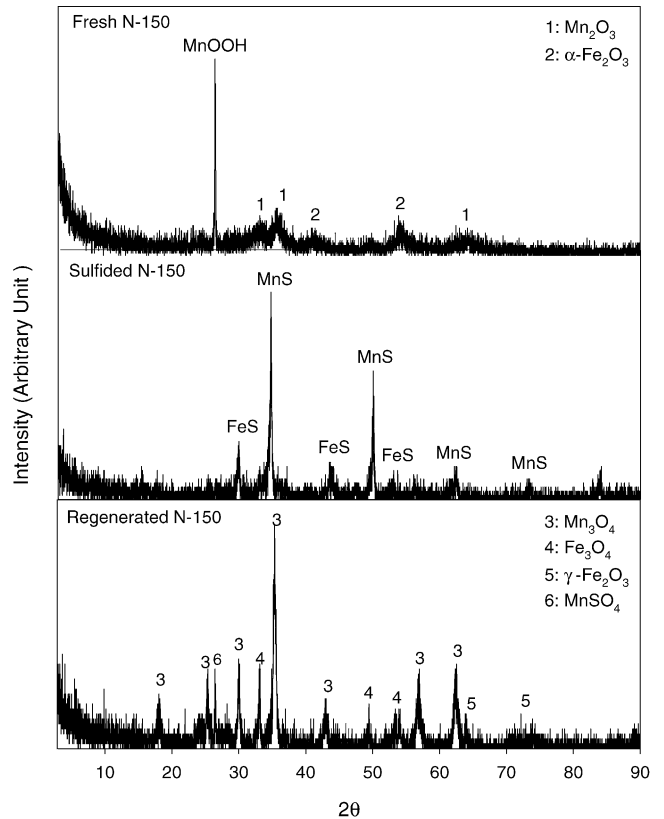


Fig. 8. X-ray powder diffraction patterns of fresh, sulfided and regenerated N-150 sorbents.

poor crystalline phases are also found on manganese oxide at 2θ = 32.22 and 66.18°. Following the sulfidation experiment at 773 K, the XRPD peaks indicate that all metal oxides in fresh sorbent are converted into metal sulfide. These peaks are identified only present as FeS and MnS by careful checking JCPDS files. Other metal sulfides such as FeS₂ or MnS₂ are not observed. It is interesting to note that manganese sulfide peaks are significantly appearing intense crys-

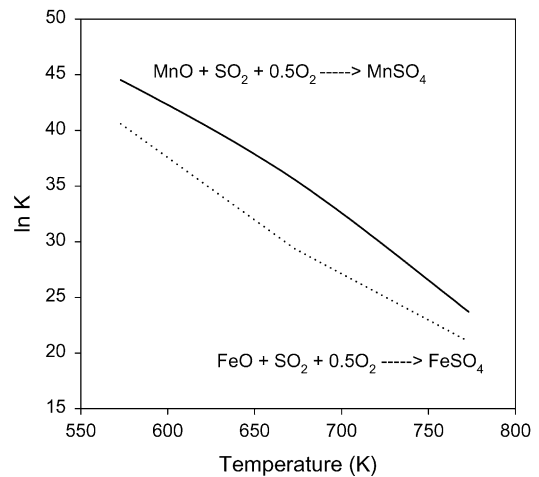
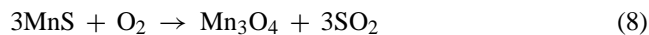


Fig. 9. Equilibrium constants of formation of sulfate for manganese and iron oxide.

talline phase while iron sulfide are poor even amorphous state. Surprisingly, after exposing to dilution air for N-150 regeneration, it indicates that the chief of active species are Fe_3O_4 and Mn_3O_4 . The regenerated N-150 peaks in XRPD pattern became more intense than those of the fresh N-150 sorbent. According to above results it is concluded that regeneration reactions are taking place through the following reaction:



In the case of regenerated sorbent, a special peak at $2\theta = 24.13^\circ$ was found and this peak was defined as MnSO_4 . This is because, under high temperature a portion of metal sulfide is transferred into metal sulfate in presence of oxygen and causes incomplete regeneration [12]. The formation of manganese sulfate could be expressed through suggested following two-step reactions:



It is interesting to note that metal sulfate is mainly associated with Mn (MnSO_4) not with Fe (FeSO_4). To explain this

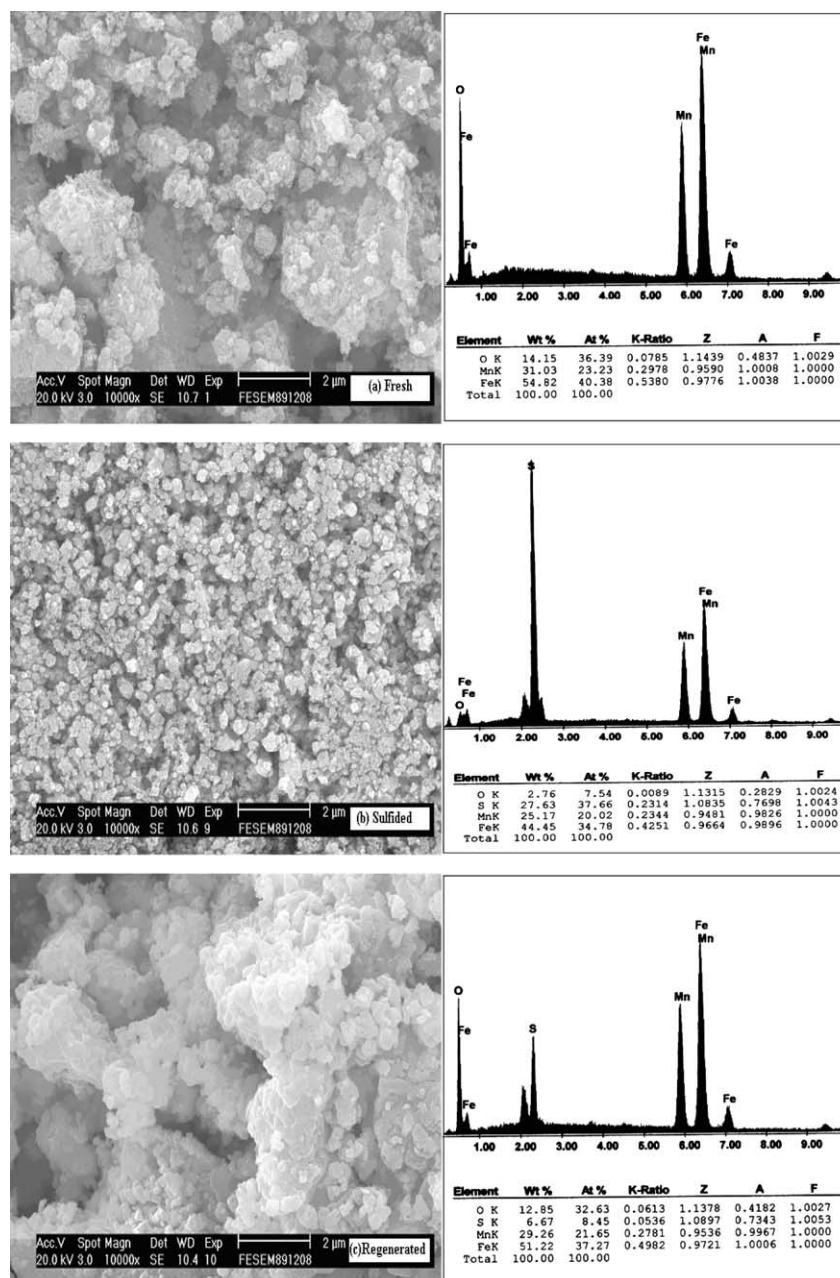


Fig. 10. SEM morphologies and EDS spectra of fresh, sulfided and regenerated N-150 sorbents.

result, the equilibrium constant for MnSO_4 and FeSO_4 were calculated based on thermodynamic. Fig. 9 plots the equilibrium constants as a function of temperatures for MnSO_4 and FeSO_4 . It is clearly to show that the equilibrium constants for MnSO_4 and FeSO_4 are very vast, indicating that the sulfate formation is favorable. The equilibrium constants decrease with temperature for two cases. High temperature leads to both reactions become unfavorable. Compared to two cases, it is obvious that the equilibrium constant of MnSO_4 is greater than that of FeSO_4 in the temperature ranges. This implies that the formation of MnSO_4 is favorable than FeSO_4 . So, after regeneration only MnSO_4 was found. However, FeSO_4 or MnSO_4 sulfate formation has been regarded as one of the most serious problem during regeneration progress. It is believed that increasing regeneration temperature or decreasing oxygen concentration may be the best way to overcome sulfate formation.

SEM morphologies and EDS spectrum of fresh, sulfided and regenerated N-150 sorbents are shown in Fig. 10. There is a noticeable observation in fresh and sulfided N-150 sorbent. In the case of sulfided sorbent, drastic changes occurs after 773 K sulfidation, where small and very dense dispersion were observed. This is because that after sulfidation process, metal oxides were converted by H_2S to metal sulfides. After regenerated at 773 K, it can be found that particles agglomerate apparently and strikingly differ from that of fresh sample. This finding attributes to a slight sintering effect. In fact, regeneration is an extreme exothermic reaction ($\Delta H_{773\text{K}} = -1638.6 \text{ kJ/mol}$). During regeneration progressing at 773 K the internal temperature may be up to 873 K. Under such high temperature it is plausible to cause sintering effect. To understand the extent of sintering effect, fresh and regenerated N-150 sorbents were conducted to analyze their surface area and pore structure. Results indicate that the BET surface area does not appear a huge change before and after regeneration. Only about 11% BET surface area is lost after regeneration (129.1 and 115.3 m^2/g for fresh and regenerated N-150 sorbent, respectively).

Furthermore, the EDS spectrum for fresh sample indicates that Mn and Fe are main components. Amounts of oxygen content are approaching to 14.15%. After sulfidation, the amounts of oxygen content are decreasing to 2.76% and obviously that amounts of sulfur is detected in sulfided sample. Results indicate that oxygen are replaced by sulfur and then formed MnS and FeS . On the other hand, in the case of the regenerated sorbent, amounts of oxygen content are increasing to 12.85%. It is also observed that sulfur present in regenerated sample, indicated that sulfur present as metal sulfate form. These findings correspond with the result of XRD, in which shown that MnSO_4 was detected in regenerated sample. Combination with the results of XRD and SEM/EDS, sulfate formation and sintering effect are major reasons to cause active loss in sulfidation/regeneration cycle. In particular, sulfate formation is more series than a loss of surface area in regeneration process.

4. Conclusions

High temperature removal of hydrogen sulfide by using N-150 sorbent was conducted in a bench scale fixed bed reactor. The results show that N-150 sorbent is capable of achieving less than 10 ppm H_2S concentration in effluence stream with a significant sorbent utility prior to breakthrough in appropriate operation condition. In the temperature range of 673–873 K, it is shown that the sulfur capacity is increased with reaction temperature for N-150 sorbent. The sulfur capacity is approaching to theoretical value at 873 K in the operation range. After regeneration, the sulfur capacity maintains approximately 85% utilization compared to the fresh sample. There is no significant huge deterioration for regenerated N-150 sorbent. The sulfur capacity is related with CO and H_2 content. CO is a positive effect, while H_2 is negative effect. This result can be explained via water-shift reaction. From the analysis of XRD, an undesired MnSO_4 peak is found after regeneration. By further analysis of EDS, we also observed residual sulfur present in regenerated sample. Combination with the results of XRD and SEM/EDS, we conclude that sulfate formation and sintering effect are major reasons to cause active loss in sulfidation/regeneration cycle.

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