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Effects of addition of Mo on the sulfidation properties of Fe-based sorbents supported on fly ash during hot coal gas desulfurization

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ABSTRACT

This paper studies the influence of the addition of Mo on the sulfidation performance of Fe-based sorbent supported on fly ash for hot coal gas desulfurization. Sorbent samples were prepared using physical mixing method with different Mo oxide content. The sulfidation experiments were carried out in the temperature range of 400–600 °C. Gas compositions were analyzed using a GC. The structure and morphology of sorbent samples before and after sulfidation were examined by using SEM, XRD and compressive strength was also measured. The experimental results show that the fly ash supporter has some capability for sulfur removal from the hot coal gas. The addition of Mo may effectively improve the desulfurization efficiency and increase the compressive strength of iron-based sorbents.

1. Introduction

H_2S contained in the coal gases from gasification will be transformed into SO_2 in the subsequent combustion process, causing serious air pollution. Therefore, desulfurization of the coal gas at high temperature is crucial to gasification-based clean coal technologies. In recent years, due to the development of coal gasification-based poly-generation technology in China, hot coal gas desulfurization technologies have drawn increasing attentions [1]. High temperature coal gas desulfurization is a typical dry desulfurization, which has been researched in the past as part of the development of Integrated Gasification Combined Cycle (IGCC) and Molten-Carbonate Fuel Cell (MCFC) power generation technologies for industrial applications [2]. Current research and development of high temperature coal gas desulfurization sorbents has been mainly focused on mixed metal oxides such as iron-based, zinc-based, manganese-based oxides sorbents [3,4]. Iron oxide sorbents have been much favored because of its abundant resources, lower price, high sulfur capacity and reactivity and it is easy to be regenerated. Sorbent supporter plays an important role for performance of sorbents during desulfurization. Current sorbent supporters mostly use stable silica, alumina complex, etc. However, fly ash from coal fired power stations may also be a suitable candidate [5]. The fly ash, which is the solid waste of coal-fired power plants, is mainly comprised of silica and alumina and environmental pressure drives the utilization of fly ash worldwide [6–9]. Fly ash is chemically stable because it is formed at high temperatures. Fly ash may also pose high reactivity to the sorbents because of its well developed pore structure and greater specific surface area [10,11]. Steijins and Mars [12] studied the influence of pore structure of different substances on their desulfurization performance and found that micropore less than 0.5–1 nm had the highest catalytic activity. In our previous studies [13,14], iron oxides based sorbent supported on fly ash have shown comparably good performance during hot coal gas desulfurization. However, the desulfurization efficiency and mechanical stability needs to be improved for iron oxide based sorbents. In this paper, the influence of addition of Mo on the sulfidation performance of Fe-based sorbents supported on fly ash is reported.

2. Experimental

2.1. Sorbents preparation

Sorbents were prepared by physical mixing method, with the mixture of iron oxide and molybdenum oxide as the active components, fly ash (63–90 μm) as the supporter, kaolin as the binder. The mixture of iron oxide, molybdenum oxide, fly ash and kaolin were physically mixed after which water was added. An extruder was then used to form wet cylindrical sorbent particles with a size of $\varphi 2 \times 3$ mm. The sorbent samples were dried at 120 °C for 4 h and then calcined at 700 °C for 8 h. Mass ratio of active components, fly ash and the binder in sorbents was 4:5:2. The compositions of the sorbents are shown in Table 1. In Table 1, the molar ratio

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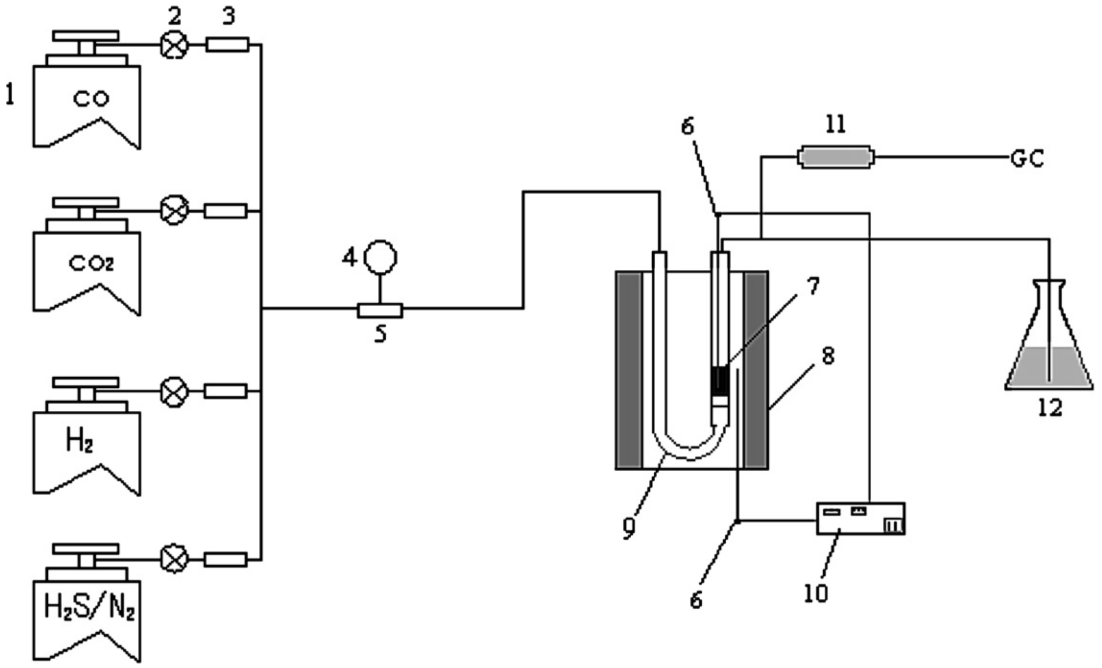

Fig. 1. Schematic diagram of the experimental set-up for sulfidation (1. gas cylinder; 2. regulator; 3.flowmeter; 4. pressure gauge; 5. mixing buffer; 6. thermocouple; 7. sorbent bed; 8. electric furnace; 9. U-tape fixed-bed quartz reactor; 10. temperature controller; 11. vacuum pumps; and 12. gas adsorption).

Table 1
Compositions of the Fe–Mo sorbent samples.

Sample no.	Sample	Mole ratio Fe_2O_3:MoO_3	Binder
S1	(F1M1)4B2A5	1:1	Kaolin
S2	(F3M1)4B2A5	3:1	Kaolin
S3	(F4M1)4B2A5	4:1	Kaolin
S4	(F5M1)4B2A5	5:1	Kaolin
S5	(F6M1)4B2A5	6:1	Kaolin
S6	(F8M1)4B2A5	8:1	Kaolin

Symbol: (F: Fe_2O_3; M: MoO_3; B: binder; and A: fly ash).

of Fe_2O_3:MoO_3 in different sorbent samples is given. Six different Fe_2O_3:MoO_3 molar ratios were used in sample 1 to sample 6 in the experiments and the samples were assigned as F1M1 to F8M1, respectively.

2.2. Experimental set-up for sulfidation

The schematic diagram of the set-up of the sulfidation experiments is shown in Fig. 1. Sulfidation experiments were carried out in the apparatus with a U-shape fixed-bed quartz reactor in the temperature range of 400–650 °C at atmospheric pressure. Simulated coal gas was used in the sulfidation experiments with the space velocity of 2000 h^{-1}, and the gas compositions are given in Table 2. Two thermocouples were used to measure the furnace temperature and sorbent bed temperature, respectively (with +1% deviation). A volume of about 25 ml sorbents was charged into the reactor in each experiment. The H_2S breakthrough time was set when its concentration exceeds 200 ppmv in the exit gas. According to the requirement of the integration of desulfurization and dust removal as well as the two phase desulfurization processes, sulfidation experiments were carried out in the temperature range of 400–650 °C. Experimental conditions during sulfidation are shown in Table 3. The gas flow rate was controlled using flowmeters with deviation about ±0.5%.

Table 2
Compositions of the simulated coal gas (vol.%).

Composition	H_2	CO	CO_2	H_2S	N_2
Concentration	39.58	32.69	19.05	0.51	Balance

Table 3
Experimental conditions used in the sulfidation experiments.

Parameters	Temperature, °C	Gas velocity, h^{-1}	Pressure, MPa
Value	400–650	2000	0.1

2.3. Analytical instruments

During sulfidation experiments, the exit and inlet gases from the reactor were analyzed using a GC equipped with a thermal conductivity detector (TCD) and a flame photometric detector (FPD). The sulfur capacity and sulfidation efficiency were defined by the following equations:

$$\text{Sulfur capacity} = \frac{\text{Sulfur absorbed (g)}}{\text{Fresh sorbents (g)}} \times 100\%$$

$$\text{Sulfidation efficiency} = \frac{\text{Inlet } H_2S \text{ (ppm)} - \text{Outlet } H_2S \text{ (ppm)}}{\text{Inlet } H_2S \text{ (ppm)}} \times 100\%$$

The morphology of the sorbent samples before and after sulfidation experiments were analyzed using a scanning electronic microscope (SEM). The mechanical strength of the sorbent was measured on a compression strength tester. The sorbents before and after sulfidation were also analyzed using an XRD to determine the transformation of the active components during sulfidation.

3. Results and discussion

3.1. Sulfidation of individual components

In order to investigate the properties of individual components of the sorbents, the sulfidation experiments were conducted on the

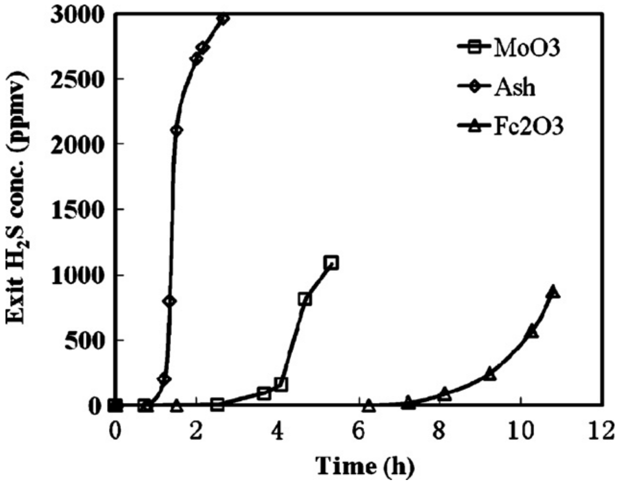

Fig. 2. Sulfidation curve of fly ash, molybdenum oxide and iron oxide.

active components with sole molybdenum oxide, iron oxide and fly ash, respectively. The sulfidation curves of the three components at 500 °C are shown in Fig. 2. From the results, it is quite apparent that iron oxides had the largest hydrogen sulfide absorption capacity while fly ash may adsorb small amount of hydrogen sulfide. The capacity of hydrogen sulfide adsorption for MoO_3 was in between. The fact that fly ash alone adsorbs hydrogen sulfide makes the fly ash as the desulfurization sorbent supporter advantageous over other inert materials such as pure alumina.

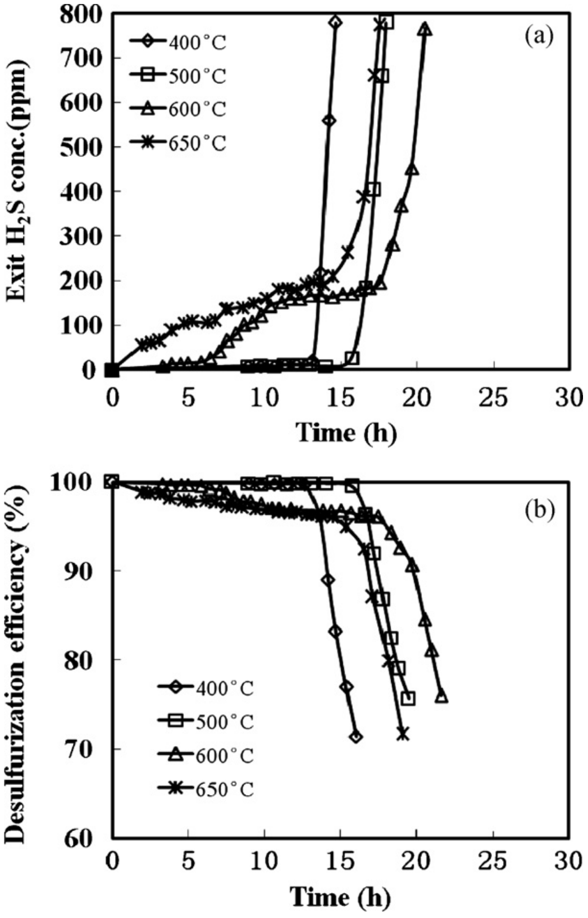

Fig. 3. Sulfidation curves of S4 sample at different temperatures. (a) Exit H_2S concentration; (b) Desulfurization efficiency.

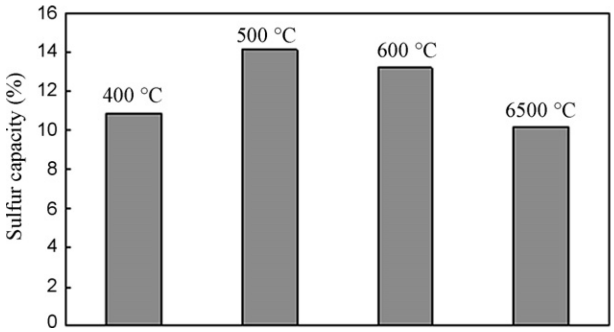

Fig. 4. Comparison of sulfur capacity of S4 sample at different temperatures.

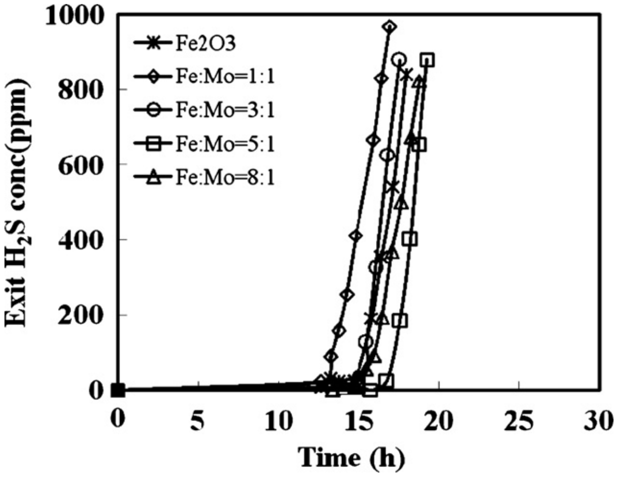

Fig. 5. Sulfidation curves of Fe–Mo based sorbents at 500 °C.

3.2. Effect of sulfidation temperature and sorbent composition

Systematic sulfidation experiments were carried out on sample S4, i.e., (F5M1)4B2A5 in which the molar ratio of Fe_2O_3:MoO_3 was 5:1 at four different temperatures, i.e., 400 °C, 500 °C, 600 °C and 650 °C. The sulfidation curves are shown in Fig. 3(a) and the desulfurization efficiency curves are shown in Fig. 3(b). From the results, it is clear that sulfidation temperature plays critical role on the performance of sorbents. The performance of the sorbent was better at 400 °C and 500 °C with longer breakthrough time and higher desulfurization efficiency, especially at 500 °C. When the sulfidation temperature was increased to 600 °C, the sulfidation performance dropped significantly. The breakthrough time was

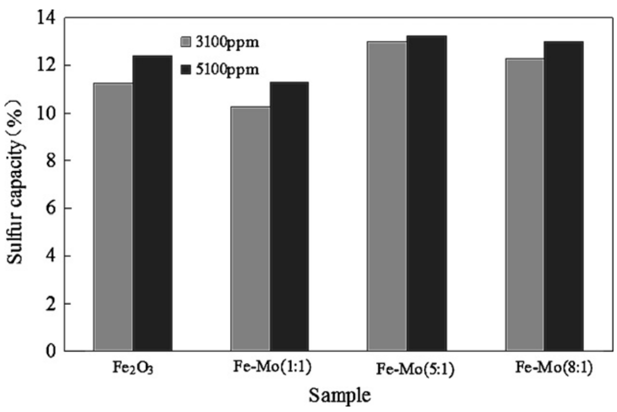

Fig. 6. Sulfur capacity of Fe–Mo based sorbents at different ratio and concentration of H_2S.

Table 4
Mechanical strength of different sorbents before and after sulfidation.

Molar ratio of Fe_2O_3:MoO_3		3:1	4:1	5:1	6:1
Mechanical strength $N\,cm^{-1}$	Before sulfidation	138.5	126.8	96.1	88.2
	After Sulfidation	156.3	131.7	108.2	91.4

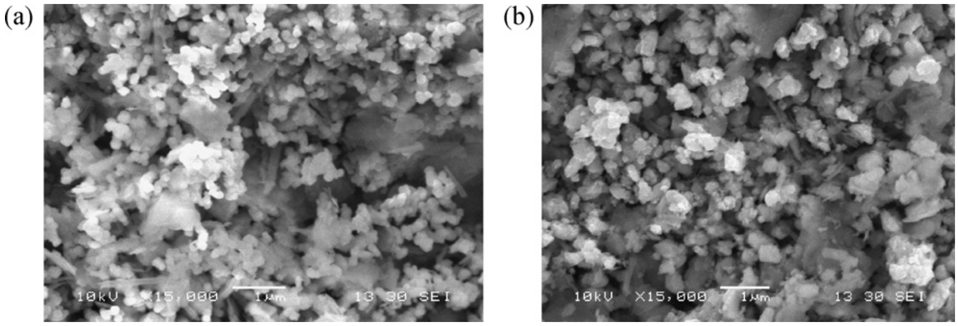

Fig. 7. SEM pictures of the sorbent of S4 (Fe–Mo ratio of 6:1)) before and after sulfidation at 500 °C. (a) before sulfidation; (b) after sulfidation.

shorter while the desulfurization efficiency was lower, as shown in Fig. 3(b). The desulfurization performance of the sorbent was the worst at 650 °C. This suggests that the Fe–Mo sorbents have the optimal performance at 500 °C. This may be attributed to the reduction of Fe oxides at higher temperatures under the strongly reduced gas environment. It has been recognized in the literature [16] that Fe_3O_4 is the intermediate phase in the overall conversion of Fe_2O_3 to FeS. At higher sulfidation temperatures such as 650 °C and in gasification product gases, the Fe_2O_3 reduction is enhanced due to the presence of H_2 and CO, leading to the formation of wustite ($Fe_{0.947}O$) and even of metallic Fe. The reactivity of wustite and metallic Fe towards H_2S is lower compared to magnetite. This may have decreased the sorbents reactivity and desulfurization efficiency in the present study.

The sulfur capability of the S4 sample during desulfurization at different temperatures was calculated and is compared in Fig. 4. The results indicate that the desulfurization activity of the S4 sorbent was different at different temperatures with the maximum sulfur capacity at 500 °C. The drop in the sulfur capacity at higher temperatures (such as 600 °C and 650 °C) were believed to be due to the reduction of iron oxides at higher temperature in the strong reducing environment gases and this leads to a much lower reactivity of the sorbents towards hydrogen sulfide. In the meantime, when sulfidation temperature was higher than 500 °C, the sulfidation efficiency decreased. This may be attributed to sintering of the sorbents as sulfidation temperature was increased due to the heat generated by the sulfidation reaction. Consequently, this resulted in the reduction of the surface area of sorbents. Therefore, desulfurization activity of the sorbents decreased correspondingly at temperatures higher than 600 °C.

Effects of the molar ratio of Fe_2O_3:MoO_3 on the sorbents performance were investigated at 500 °C and the results are shown in Fig. 5. During calcinations process, the Fe_2O_3 and MoO_3 will form the complex compounds. Therefore, the molar ratio of Fe_2O_3:MoO_3 will determine the form of Fe and Mo in the sorbent after calcination, i.e., the amount of $Fe(MoO_4)_3$, Fe_2O_3 or MoO_3. It was reported

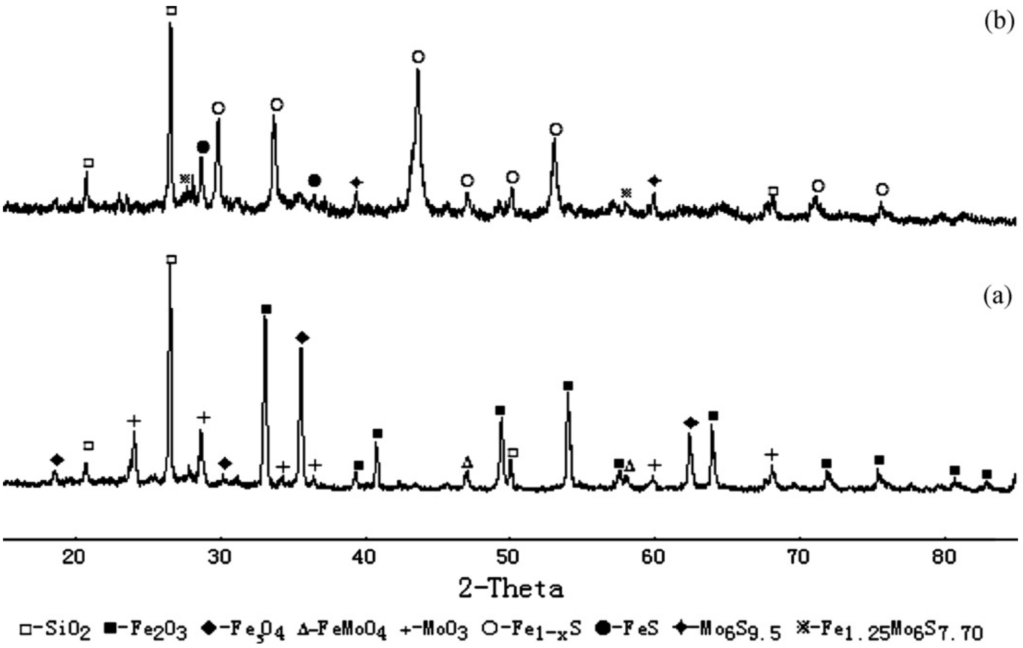

Fig. 8. XRD patters of sorbents before and after sulfidation at 500 °C.

[15] that iron oxide and molybdenum oxide can form $Fe_2(MoO_4)_3$ during calcination. Increasing the amount of MoO_3 in the sorbent and good mixing would increase the amount of phase $Fe(MoO_4)_3$. From Fig. 5, it is quite obvious that the molar ratio of Fe_2O_3:MoO_3 significantly influences the sorbent performance during sulfidation and improved both sulfur capacity and desulfurization efficiency. Overall, the addition of Mo greatly improved the sorbent performance at 500 °C. There is an optimum molar ratio of Fe_2O_3:MoO_3, and the ration of 5:1 gives the longest breakthrough time at 500 °C. The sulfur capacity was highest at 500 °C when the ratio of Fe to Mo was 5:1. However, the effect of the addition of Mo on the sulfur capacity of the sorbent samples was not as significant as on desulfurization efficiency. During sulfidation experiments, with the addition of Mo, the exit concentration of H_2S was hardly detectable with GC compared to the cases without addition of Mo.

The effects of H_2S concentration on desulfurization efficiency of Fe–Mo sorbents during sulfidation were investigated at 500 °C and the results are shown in Fig. 6. The increase in the inlet concentration of H_2S slightly increased the sulfur capacity of all the sorbents, i.e., sulfur capacity was slightly higher when the inlet concentration of H_2S was 5100 ppmv than that in the 3100 ppmv with all the samples. However, the increase in the sulfur capacity for the ration of 5:1 was the least. This is because that higher inlet concentration of H_2S results in a higher mass diffusion flow of the H_2S to the surface of the active components and increased the conversion of the sorbents.

3.3. Sorbents mechanical strength and SEM analysis

The mechanical strength of the sorbents at different mole ratio of Fe_2O_3:MoO_3 was measured before and after sulfidation at 500 °C and the results are shown in Table 4. It can be seen that the mechanical strength of the sorbents increased when more Mo was added into the sorbents. It is therefore clear that the addition of Mo oxide may significantly improve the mechanical strength of the sorbents after calcination. Moreover, the addition of Mo improved the mechanical strength of the sorbents after sulfidation with the mole ratio of Fe_2O_3:MoO_3 of 3:1 to 6:1. Therefore, the addition of Mo oxide is effective to improve the performance of Fe-based sorbents during hot coal gas desulfurization at this temperature. In practical cases, fragmentation may become a problem for dry hot coal gas desulfurization. In particular, fluidized-bed reactor systems will be the dominant approach to achieve better efficiency and better heat transfer in bed. Fragmentation of sorbents during desulfurization is caused by chemical reactions between the sorbent and reactant gases, crystallization of sorbent components, mechanical attrition and thermal shock during heat/cooling processes during sulfidation/regeneration cycles. Increase in the mechanical strength will reduce the fragmentation of sorbents during desulfurization processes.

SEM images of the sorbent of S4 with Fe–Mo ratio of 6:1 before and after sulfidation at 500 °C are shown in Fig. 7. Under SEM, no apparent morphological changes seems to have taken place during sulfidation at 500 °C, even though the sorbent color after sulfidation changed from red to black under naked eyes. This suggests that the Fe–Mo sorbents supported on fly ash may have stable properties during sulfidation.

3.4. XRD analysis

XRD patters of the S4 sorbent sample before and after sulfidation are shown in Fig. 8(a) and (b). It can be seen that the active components of Fe–Mo sorbents prior to sulfidation exists as Fe_2O_3 and MoO_3 with small amount of $FeMoO_4$ and magnetite. In the sulfidated sorbents, Fe and Mo existed as $Fe_{(1-x)}S$, FeS, $Mo_6S_{9.5}$, $Fe_{1.25}Mo_6S_{7.7}$. We believe that the following overall sulfidation reactions have taken place.

$$(1-x)Fe_2O_3 + 2H_2S + (1-3x)H_2$$

$$/CO \rightarrow 2Fe_{(1-x)}S + 3(1-x)H_2O/CO_2$$

$$MoO_3 + 2H_2S + H_2/CO \rightarrow MoS_2 + 3H_2O/CO_2$$

The resulting high temperature phases are partly transformed to low temperature phases during cooling of the products. For instance, iron sulfide during sulfidation at high temperature exists as $Fe_{(1-x)}S$ (pyrrhotite). As the temperature is decreased, $Fe_{(1-x)}S$ is transformed into FeS (troilite). However, because the cooling rate was quick, the system did not reach equilibrium and the iron sulfur compounds in the sulfidated sorbents existed as the mixture of $Fe_{(1-x)}S$ and FeS. This is consistent with the thermodynamic study on Fe–S system by Waldner et al. [17]. Small amount of complex compound is also present. It can be also seen that the reaction and transformation of the metal oxides species were quite complicated.

4. Conclusions

The addition of Mo oxide can significantly improve performance of the iron-oxides based sorbents supported on the fly ash through the promotion of their desulfurization efficiency, sulfur capacity and the optimum mole ratio of Fe and Mo is 5:1. The best sulfidation temperature for Fe–Mo based sorbents supported on fly ash in this study was 500 °C above which the desulfurization performance dropped greatly. The addition of Mo oxide also improved the mechanical properties of the Fe-based sorbents after sulfidation.

Acknowledgements

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