The Effects of CeO₂ Addition on the Performance of Zinc Oxide Sorbent Prepared by Microwave Solid-State method for H₂S Removal

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Abstract. ZnO sorbents with different CeO₂ loadings were prepared by microwave calcination and tested the performance for H₂S removal in a fixed-bed reactor at 500 ℃. The results revealed that the Ce-doped sorbents have a higher efficiency and longer breakthrough time compared with non-modified sorbents. The optimal sulfur capacity (13.03 gS/100 g) and breakthrough time (17.5 h) were obtained when the content of CeO₂ up to 4 wt.%. XRD, SEM, XPS and mercury porosimetry methods were used to characterize the structure of sorbents. Analysis data indicated that the addition of CeO₂ leads to better pore structure and larger specific surface, which facilitates the diffusion of H₂S into the active sites. Furthermore, the presence of CeO₂ also results in an increase in the content of surface elements including Zn and O, which contributes to improve the ability of H₂S removal.

Introduction

The integrated coal gasification combined cycle (IGCC) process is considered as one of the promising clean coal technologies in the 21st century [1-3], meanwhile the high temperature gas desulfurization (HTGD) was regarded as one of the key techniques in the IGCC system [2-7]. The oxides of Zn, Fe, Ca, Mn and Co as H₂S sorbents for HTGD are investigated extensively nowadays [7-13].

Among these sorbents, Zinc oxide sorbents are considered to be the most promising material for HTGD because of its large sulfur capacity and excellent desulfurization thermodynamics [7, 14, 15]. Up to now, many synthesis methods have been investigated [16-20]. In comparison with traditional preparation methods, microwave irradiation is a burgeoning method to prepare desulfurizer by virtue of it can provide a rapid drying and evenly heating [21]. The advantages of microwave heating over conventional heating have been studied in our previous work [22].

But under the condition of high temperature, the ZnO sorbents would evaporate thus limit its development [7, 23]. Moreover, single ZnO sorbents show many disadvantages such as decrease of sorbent efficiency and degradation of the mechanical properties [24]. In order to improve the performance, ZnO sorbents mixed with many metal oxides have been evaluated [24-27]. CeO₂ as one of the most promising rare earths has an outstanding oxygen storage capacity and improve the performance of ZnO sorbents for desulfurization [11, 28-30].

In this paper, the performance of ZnO based sorbents doped with various content of CeO₂ employed for high temperature coal gas desulfurization were studied. Also, the effects of the amount of CeO₂ loaded to the sorbents on the performance for H₂S removal were studied. The analysis data of structure and textural properties were provided by XRD, XPS, SEM and mercury porosimetry.

Experiment

Preparation of Sorbents. All sorbents were prepared by solid-state method. First, $(CH_3COO)_2Zn\bullet 2H_2O$ and $H_2C_2O_4\cdot 2H_2O$ were grinded in a mortar at a molar ratio of 1:1, and then the reaction mixture was mixed in a planetary ball mill for 2 h. The precursor was calcined at 450 ℃ after dried for 10 h at 80 ℃ to get the active component nano-ZnO. After mixed up with a certain amount of CeO₂ as promoter, the nano-ZnO prepared was mixed thoroughly with modified semi-coke and

kaolin in a high-energy planetary mill (QM-3SP2) at the rotation rate of 350 r/min for 2 h. Afterwards, the water was added to the system and the paste obtained was extruded into a cylindrical shape ($\Phi 3 \times 3$ mm). After dried at 100 ℃，the resulting product was transferred into a microwave oven and calcined at 500 ℃ for 1 h under N_2 atmosphere. In this paper, the loading amount of CeO_2 was 0, 4, 8, 12 wt.%, and the corresponding samples were denoted as ZSC0, ZSC4, ZSC8 and ZSC12, respectively.

Desulfurization Tests of Sorbents. The desulfurization performance of sorbents was tested in a fixed-bed quartz reactor at 500 ℃ with a space velocity of 2000 h^{-1}. About 10g sample was placed in the middle of the quartz tube. The composition of the simulated coal gas was H_2 (39 vol%), CO (27 vol%), CO_2 (12 vol%), H_2S (2700 ppm) and N_2 (balance). The outlet concentration of H_2S was analyzed by a gas chromatography (GC-950, Shanghai Haixin chromatography Instrument Co., Ltd.) equipped with a flame photometry detector (FPD). The breakthrough time was defined as the time when the concentration of H_2S in outlet gas reaches 500 ppm. The sulfur capacity was the mass of sulfur absorbed per 100 g sorbents.

Characterization of the Sorbents. The structures of the sorbents were determined by X-ray powder diffraction (XRD) using a Rigaku D/max-2500 with Cu Kα radiation (λ = 1.5418 Å) operating at 40kV and 100mA in the 2θ range from 10° to 80°. The morphology of the samples was observed by Scanning electron microscopy (SEM, JSM-6700F). The X-ray photoelectron spectroscopy (XPS) spectra of the sorbents were obtained using a photoelectron spectrometer (ESCALab220i-XL) with Al Kα source at 300W. The textures of the sorbents were measured with a mercury porosimetry (PORESISER-9320, Micromeritics Co., USA).

Result and Discussion

Desulfurization Tests. The breakthrough curves of the sorbents with various amount of CeO_2 are shown in Fig.1 and the sulfur capacities are shown in Fig.2. Compared with the ZSC0, the sorbents doped with CeO_2 have better performance for desulfurization demonstrating that the loading of CeO_2 uprate the properties of sorbents. The longest breakthrough time (17.5 h) and the highest sulfur capacity (13.03 g) are obtained when the amount of CeO_2 lived up to 4 wt.%. The phenomenon observed may attribute to the different characteristics of structure.
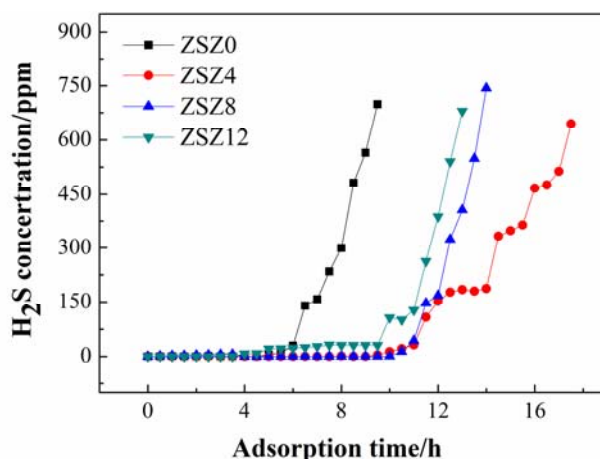

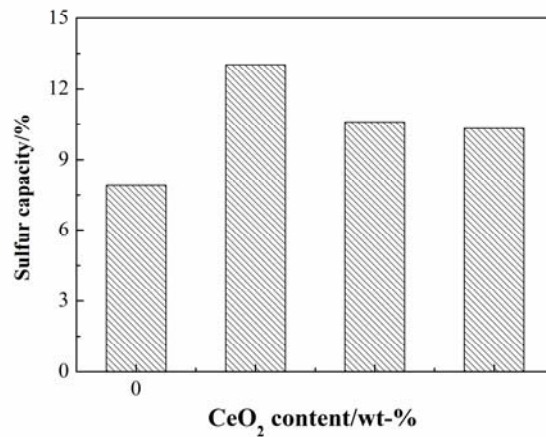
Figure 1. Effect of content of CeO_2 on breakthrough curve

Figure 2. Effect of content of CeO_2 on sulfur capacity

XRD Analysis. The XRD patterns of the sorbents with different content of CeO_2 are shown in Fig.3. The results show that the characteristic peaks of CeO_2 were observed in the pattern of ZSC4, ZSC8 and ZSC12, and the position of ZnO crystal peak didn't shift with the amount of CeO_2 indicating that the crystal structure of ZnO has not been transformed caused by the addition of CeO_2.

It is found that the intensity of ZnO crystal peaks becomes stronger and sharper with the increase of CeO_2. In according with the pattern of XRD, the average particle sizes of all samples were estimated on the basis of Scherrer formula. The calculated results show that the average particle sizes of sorbents with different addition of CeO_2 are 9.2, 17.6, 30.2 and 32.1 nm corresponding to the ZSC0, ZSC4, ZSC8 and ZSC12 sorbents, respectively. The smaller crystal size triggered a better dispersion of active component and increased the active sites of desulfurizer, resulted in a superior performance for H_2S removal [27]. This conclusion is consistent with the experimental result that the ZSC4 sorbents have the best desulfurization properties among these sorbents.
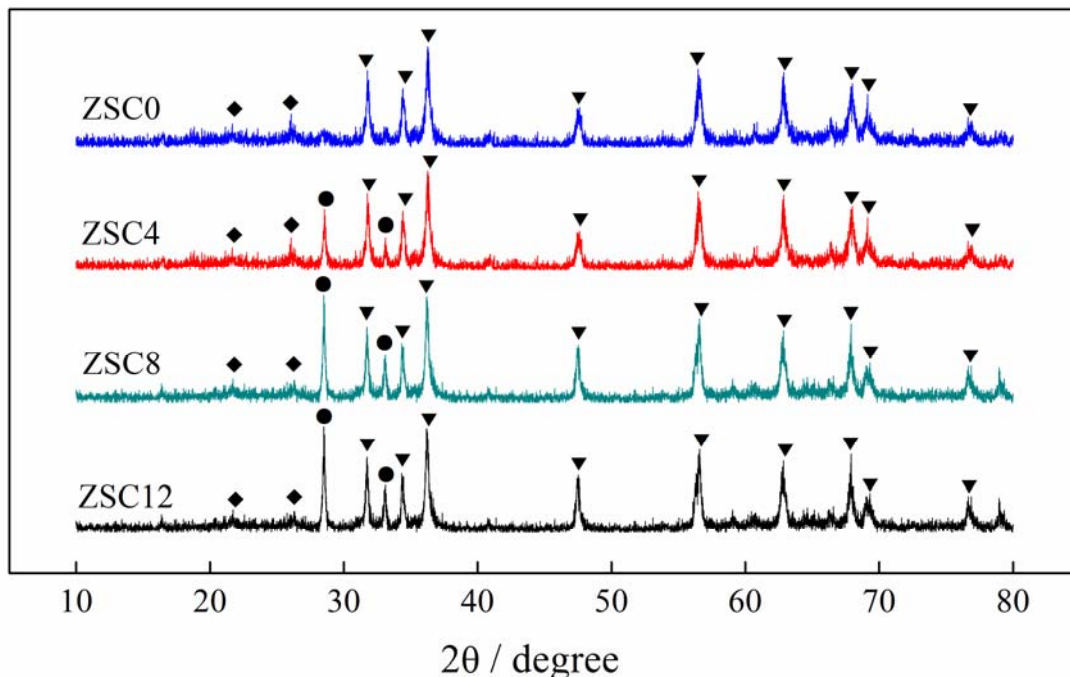

Figure 3. XRD patterns of sorbents obtained with different content of CeO_2
●---CeO_2 ▼---ZnO   ◆---SiO_2

Pore Structure Analysis. The pore structure parameters of the fresh sorbents were investigated by a mercury porosimetry and are shown in Table 1. As shown in the Table 1, the surface area and pore

volume of the ZSC4 sorbents increase remarkably compared with the ZSC0 sorbents, indicating that CeO_2 doping improves the textural properties and resists the sintering of the sorbents [30]. In addition, from the listed data, it can be seen that the specific surface area and pore volume declined with the increase of loading amount of CeO_2 consecutively. It may due to the fact that the ionic radius of Ce^{4+} (87 pm) is larger than Zn^{2+} (74 pm). Therefore, only the appropriate addition of CeO_2 can enhance the structural performance of sorbents.

Table 1. Pore structure parameters of sorbents with different content of CeO_2

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)
ZSC0	3.162	0.123
ZSC4	8.863	0.277
ZSC8	6.321	0.182
ZSC12	5.213	0.167

SEM Analysis. The morphologies obtained by SEM of ZSC0 and ZSC4 sorbents are shown in Fig.4. As shown in Fig.4, compared with the ZSC0 sorbents, the ZSC4 sorbents have less agglomeration of the particles and smaller size of crystal, thus the active components disperse evenly on the modified semi-coke support. Meanwhile, the ZSC4 sorbents exhibit a preferable pore texture and layered-structure at a relatively loose state which is beneficial for the mass transfer during desulfurization process. These changes match well with the result of pore structure analysis.
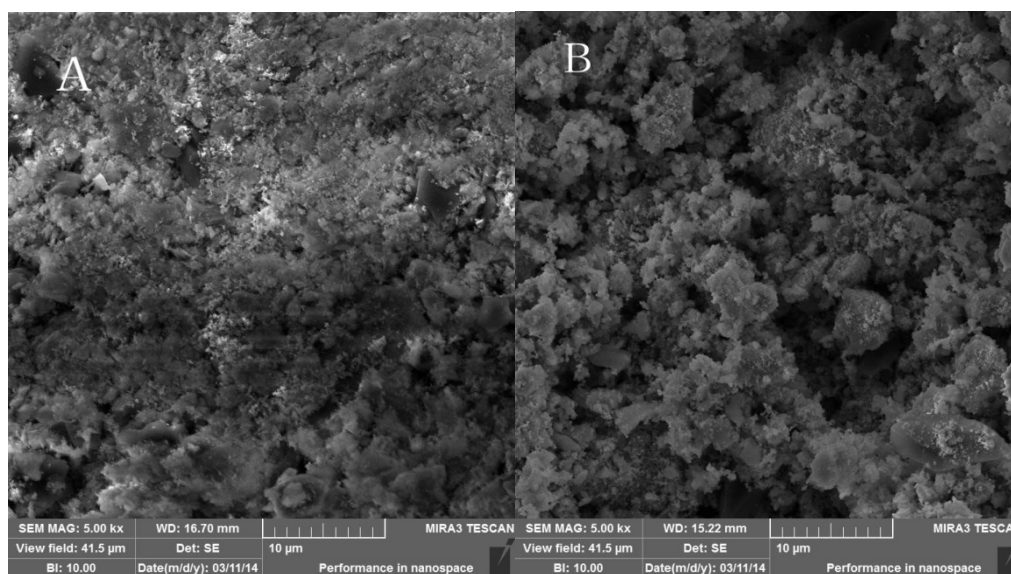

Figure 4. SEM images of the sorbent
A-0% B-4%

XPS Analysis. The chemical states of the surface species for fresh ZSC0 and ZSC4 sorbents are investigated by XPS. The XPS spectra of Zn2p of the sorbents are shown in Fig.5. As shown in Fig.5, the binding energy of Zn $2p_{3/2}$ for the ZSC0 is 1022.1 eV corresponding to ZnO. Meanwhile, the peaks of the ZSC4 appear around 1021.4 eV. The shift of binding energy before and after CeO_2-doping indicates that the addition of CeO_2 has an effect on the chemical state of ZnO and the variation can be attributed to the electronic rearrangement on account of the fact that Zn (1.65) is more electronegative than Ce (1.12), which results in a higher electron density in the periphery of Zn atom and a lower binding energy [30]. These can facilitate the absorption of acid gas. Therefore the sorbents with CeO_2 have more activity for H_2S removal.

The O1s XPS spectra of the sorbents are presented in Fig7. The binding energy of ZSC0 sorbents is 531.3 eV and the peak shifts to 530.4 eV for the ZSC4 sorbents. The phenomena indicates that

higher electron density is existed in the ZSC4 sorbents. Furthermore, as shown in Table 2, the elements Zn and O appear much more on the surface of ZSC4 than ZSC0.

The spectra of Ce 3d in the ZSC4 sorbents is shown in Fig.6. It can be seen that there are three obvious peaks of binding energy occurring at 882.4 eV, 900.8 eV and 916.7 eV, indicating the presence of CeO_2 in the sorbents.
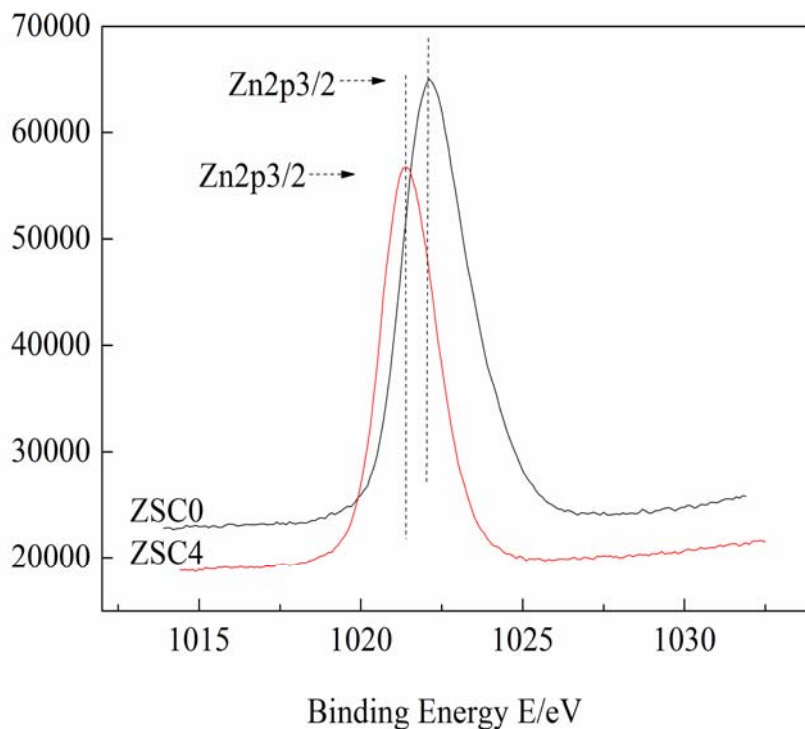

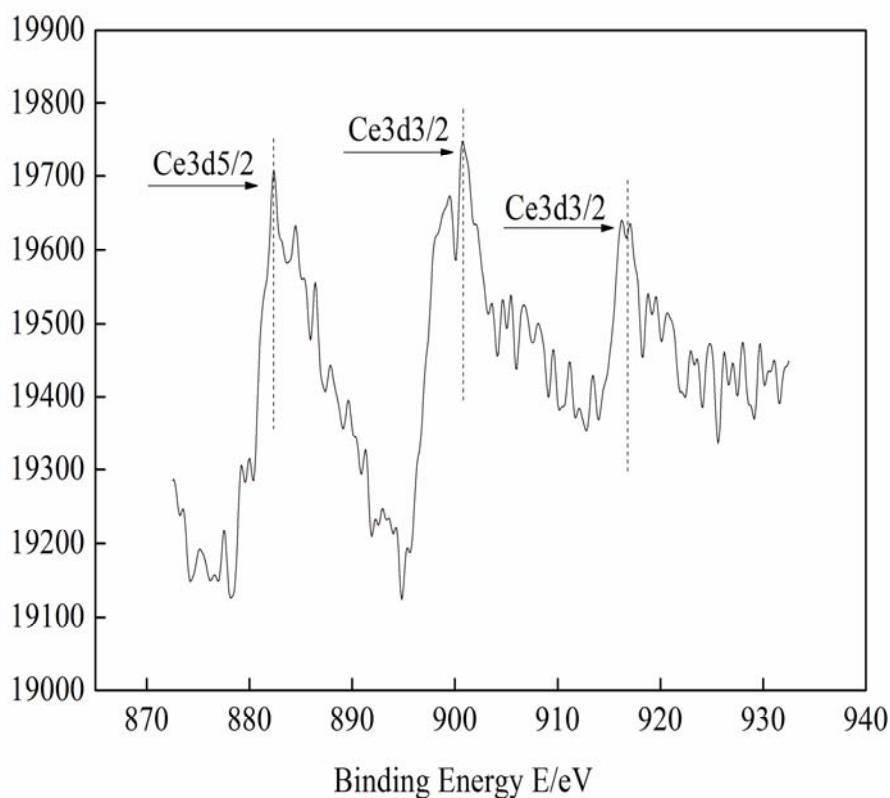Figure 5. Zn2p XPS spectra of ZSC0 and ZSC4

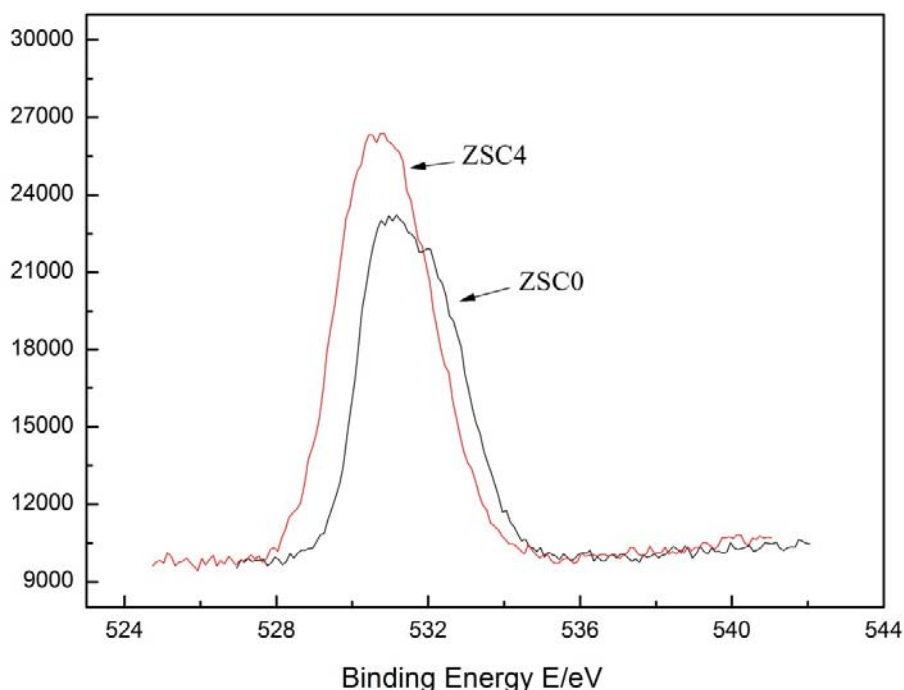

Figure 6. Ce 3d XPS spectra of ZSC4

Figure 7. O 1s XPS spectra of ZSC0 and ZSC4

The element concentrations on the surface of sorbents are exhibited in Table 2. As seen that the concentrations of oxygen and zinc in the ZSC4 are much higher than ZSC0. The higher content of active component on the surface, as well as the higher electron density, leads to a better performance of the ZCS4 sorbents for desulfurization.

Table 2. Surface composition and content of sorbents from XPS analysis

Sample	Zn, wt-%	Ce, wt-%	O, wt-%
ZSC0	5.03	0.00	17.98
ZSC4	9.01	0.41	34.03

Conclusion

The ZnO sorbents doped with different amount of CeO_2 were prepared by microwave solid-state method. The largest sulfur capacity (13.03g S/100g) and the longest breakthrough time (17.5h) were obtained when the loading of CeO_2 is 4wt.%. The results show that the appropriate addition of CeO_2 can promote the performance of ZnO sorbents for desulfurization due to the CeO_2 modifies the structure of the sorbents by increasing the surface area and the pore volume which provide more active sites and a better dispersion of active components for the sorbents. Moreover, the presence of the CeO_2 resulted in an increase of the elements including Zn and O on the surface, which is conductive to the adsorption of the H_2S.

Acknowledgements

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