Simultaneous High-temperature Desulfurization and Removal of Particulates with ZnO Dispersed Ceramic Filters

T. C. Wang[*], H. Y. Kang[*], H. Paul Wang[*] and Chih-Ju G Jou[**]

[*]National Cheng Kung University, Tainan, Taiwan, wanghp@mail.ncku.edu.tw
[**]National Kaohsiung First University of Science & Technology, Kaohsiung, Taiwan, george@ccms.nkfust.edu.tw

ABSTRACT

Flue gas cleaning at high temperatures can increase thermal efficiency with more importantly to simplify processes and lower cost. The main objective of this work was to investigate the feasibility of simultaneous desulfurization and particulate removal using ZnO dispersed ceramic filters (ZnO/CF). At the temperatures of 873-1073 K, removal efficiencies of particulates and H_2S (1%) from a simulated gas with ZnO/CF are greater than 97%. Note that ZnO on CF has little influence on its particulate filtration efficiency. Observed by synchrotron X-ray absorption near edge structure spectroscopy, about 96% of ZnO on CF can be regenerated with air at 873 K. During desulfurization, the bond distance of Zn-(S)-Zn (the 2nd shell) is increased by 0.10 Å if compared with that of Zn-(O)-Zn. Regeneration can resume the Zn-(O)-Zn bond distance to 3.20 Å.

Keywords: desulfurization, XANES, EXAFS, particulate

1 INTRODUCTION

Significant advances toward the availability of clean coal energy systems through development of integrated gasification combined cycles (IGCC) have been reported [1-7]. The IGCC engineering concepts are based on pressurized gasification, followed by combustion of product syngas in gas turbines. A steam turbine also recovers energy from the hot exhaust syngas. Regenerable absorbents are frequently used in desulfurization of a pre-quenched raw syngas. The main drawback for rapid cooling of the hot raw syngas exited from a gasifier for desulfurization, and followed by combustion of the cleaned syngas at high temperatures for power generation may lead to at least 5% reduction of the overall thermal efficiency [5].

In addition to main gas components (N_2, H_2, CO, CO_2, H_2O and CH_4) in the flue gas, particulates (char, ash), tars (polyaromatics), NH_3 and sulfur (H_2S, COS) compounds are frequently found. Particulates may cause plugging and abrasion of downstream piping and equipments, while tars may lead to blinding of ceramic filters, pipe plugging and soot formation during combustion in gas turbines or engines. Nitrogen and sulfur compounds are converted to NO_x and SO_x, respectively during combustion of a syngas. Thus, cleaning of a hot gasification raw syngas is essential for reliable and environmentally-sound operations. Effective removal of particulates and sulfur from the hot syngas is the key to success of these highly efficient advanced coal energy technologies.

Ceramic filters have been found very effectively in removal of particulates from flue gases at high temperatures. Rigid ceramic filters were utilized in combustion and gasification of coal for environmentally clean power generation in the early 1980s [6]. Direct applications of high-temperature particulate controls with ceramic filters are expected to be beneficial not only to the advanced fossil fuel processing technologies, but also to selected high temperature industrial and waste incineration processes [1].

Advanced particle filtration systems using ceramic honeycomb filters for cleaning hot gases have been developed [8]. The honeycomb filters are applicable to hot gas cleaning and dust collection, and possesses a high filtering area per volume. The filters has external dimensions of 150 mm^2 × 500 mm with a pore size of 15 μm and filtering area density of 145 m^2/m^3. Groups of honeycomb filters are periodically cleaned by a rapid (reverse-air flow) back-pulse procedure to remove the dust cake that builds up on the filter surfaces. Extensive reviews of gas cleanup at high temperatures include candle filters together with progress and issues concerning the hot-gas filtration in connection with IGCC or pressurized fluidized-bed combustion [3-5, 7-10].

Effective absorbents dispersed on porous ceramic filters can achieve the goal of simultaneous desulfurization and removals of particulates at high temperatures [11]. The absorbents like ZnO can be deposited on the virgin filters. Thus, the main objective of this work was to investigate the feasibility for simultaneous desulfurization and removals of particulates from a syngas at high temperatures. Specifically, a molecule-scale synchrotron X-ray absorption spectroscopic method was used to reveal inter-conversion of ZnO and ZnS on filters during desulfurization and regeneration at high temperatures.

2 EXPERIMENTAL

For simultaneous desulfurization and removals of particulates, ZnO (20%) supported on ceramic filters (ZnO/CF) were prepared by impregnation of 0.2 M $Zn(NO_3)_2$ (Merck) onto ceramic filters (Cerafil XT-650). The ZnO/CF sample was dried at 378 K for 8 h and calcined at 873 K for 2 h before testing. The experiments for simultaneous desulfurization and removals of particulates from simulated gases at high temperatures measured with a K-type thermocouple were carried out on a fixed-bed steel reactor (1 inch in diameter). Particulates carried by a 1% H_2S/N_2 flow (50 mL/min) were fed into the reactor. A FTIR gas cell was used to monitor the off gas. About 1.5 g of ZnO/CF were used in desulfurization as well as removals of particulates at 873-1073 K. After desulfurization, regeneration was conducted with air (50 mL/min) at 873-1073 K. The volume space velocity (STP) for desulfurization and regeneration was 6000 mL/g · h.

The XRD measurements of samples were carried out on a diffractometer (Bruker, D8 Advanced) with a Cu Kα□radiation scanned from 10 to 80° (2θ) at a scan rate of 3°/min. XANES spectra of zinc were recorded on the Wiggler (17C) beam line at the Taiwan National Synchrotron Radiation Research Center. The electron storage ring was operated at energy of 1.5. A Si(111) double-crystal monochromator was used for selection of energy. The energy resolution (ΔE/E) of the beam line was about $1.9x10^{-4}$ (eV/eV). Photon energy was calibrated by characteristic preedge peaks in the absorption spectrum of a Zn foil (9679 eV). The standard deviation calculated from the averaged spectra was used to estimate the statistical noise and error associated with each structural parameter. XANES spectra of zinc model compounds such as nano and bulk ZnO were also measured on the beam line. The X-ray absorption data were analyzed using the UWAXFS 3.0 [12] and FEFF 7.0 [13] simulated programs. The fitted pre-edged background was extrapolated throughout the data range, and subtracted and normalized to decline the effect of sample thickness. The Fourier transform was performed on k^3-weighted EXAFS oscillation in the range 3.0-11.2 $Å^{-1}$. Empirical fits of model compounds have an error of ± 0.01 Å in radius and ± 10% in coordination number (CN) for the first shell atoms.

In the temperature programmed sulfurization (TPS) (TGA TA SDT-Q600) experiments, temperatures were raised from 373 to 1073 K at a heating rate of 5 K/min under 100 mL/min of 3% H_2S/N_2. For regeneration of the sulfurized absorbents, temperature programmed oxidation (TPO) was conducted with a flowing air (100 mL/min). During TPO or TPS, off gases was monitored by FTIR (Biorad, FTS-40).

3 RESULTS AND DISCUSSION

The X-ray diffraction pattern of the ZnO/CF powder is shown in Figure 1(a). Mainly, ZnO and SiO_2 are found. The scanning electron micrograph (SEM) images of the ZnO/CF indicate that ZnO is well distributed on the ceramic filter. After desulfurization, ZnO, SiO_2, Zn and ZnS are observed (Figure 1(b)). Metallic zinc (Zn) is also observed. Mainly ZnO and SiO_2 in the regenerated ZnO/CF are found, suggesting ZnS on the CF can be oxidized completely with air at 873 K (see Figure 1(c)).

Time dependence for desulfurization with ZnO/CF at 873 K is shown in Figure 2. Little axial dispersion occurred in the desulfurization experiment as H_2S is reacted with ZnO on the CF at 873 K at the elapsed time of 2 h approximately (t/t_0=0.8-0.85).

Figure 3 shows the Zn absorption *K*-edge XANES spectra of calcined, sulfurized and regenerated ZnO/CF as well as a model compound (nanosize ZnO). A shoulder at 9665-9669 eV can be attributed to the 1s-to-4p transitions that indicates the existence of the Zn(II) species in the ZnO/CF. Interestingly, an intense feature at 9669-9673 eV for the ZnS formed from desulfurization with ZnO. The K-edge XANES spectra of the regenerated ZnO/CF are shown in Figure 3(a). The XANES spectra were also expressed mathematically in a LC XANES fit vectors, using the absorption data within the energy range 9639-9699 eV. XANES spectra of zinc and copper model compounds such as ZnO and ZnS were also measured on the SRRC Wiggler beam line. ZnO (0.96) and ZnS (0.04) are the main zinc species in the regenerated ZnO/CF.

Generally, EXAFS spectroscopy can provide the information on the atomic arrangement in terms of bond distance, coordinate number (CN), kind of neighbors, thermal and static disorder. The EXAFS spectra were recorded and analyzed in the k^2 range between 2.7 and 11.5 $Å^{-1}$. An over 99% reliability of the EXAFS data fitting for Zn species was obtained. The structural parameters obtained from the best fit to the EXAFS data are shown in Table 1. In the 1st shell of ZnO on CF, the bond distance of Zn-O is 1.94 Å with a CN of 5.6. For the 2nd shell Zn-(O)-Zn, the bond distance and CN are 3.21 Å and 8.2, respectively. Desulfurization with the ZnO/CF has caused an increase of the bond distance of Zn-(S)-Zn to 3.31 Å. In regenerated ZnO/ceramic, the bond distances of Zn-O and Zn-(O)-Zn are resumed to 1.95 and 3.2 Å.

Table 2 shows the efficiency of zinc ceramic for filtration of phosphor particulates. At the temperature range of 873-1073 K, the particulates removal efficiencies of the CF are greater than 97%. It is also clear that the coated ZnO for desulfurization may not perturb the particulates removal efficiency of the CF. At the temperature of 873 K, efficiencies of the CF experienced different flow rates containing 0.3% of particulates are shown in Table 3. With an increase of the flow rate, the filtration efficiency is decreased from 98 to 95 %. A high flow rate may cause a rapid trap of fine particles onto CF.

4 CONCLUSION

Experimentally, simultaneous desulfurization and removals of particulates at high temperatures with the ZnO/CF are very feasible. At the temperature range of 873-1072 K, removal efficiencies of particulates and H_2S from a simulated gas with ZnO/CF are greater than 97%. About 96% of ZnO is found after regeneration. Zn-O and Zn-(O)-Zn bond distances in ZnO/CF are 1.94 and 3.21Å with CNs of 5.6 and 8.2, respectively. The bond distance of Zn-(S)-Zn for the sulfurized ZnO is increased slightly by 0.1 Å. In regenerated ZnO/CF, bond distances of Zn-O and Zn-(O)-Zn are resumed to 1.95 and 3.20 Å. The combined high-temperature desulfurization and removals of particulates with the ZnO/CF system which can achieve a desired efficiency may be economically attractive especially in IGCC or coal-fired power plants.

	Shell	Bond distance (Å)	Coordination number
Oxidized	Zn-O	1.94	5.6
	Zn-(O)-Zn	3.21	8.2
Sulfurized	Zn-S	2.33	3.7
	Zn-(S)-Zn	3.31	9.6
Regenerated	Zn-O	1.95	4.4
	Zn-(O)-Zn	3.20	8.0

Table 1: Speciation of zinc in ZnO/CF after oxidation at 1073 K, sulfurization at 873 K, and regeneration at 873 K.

	Temperature (K)	Efficiency (%)
CF	873	98
	973	98
	1073	98
ZnO/CF	873	99
	973	97
	1073	99

Table 2: Particulates removal efficiencies for ZnO/CF at 873-1073 K.

	Flow rate (mL/min)	Efficiency (%)
CF	50	99
	100	98
	200	97
ZnO/CF	50	98
	100	97
	200	96

Table 3: Particulates removal efficiencies for ZnO/CF under different flow rates at 873 K.

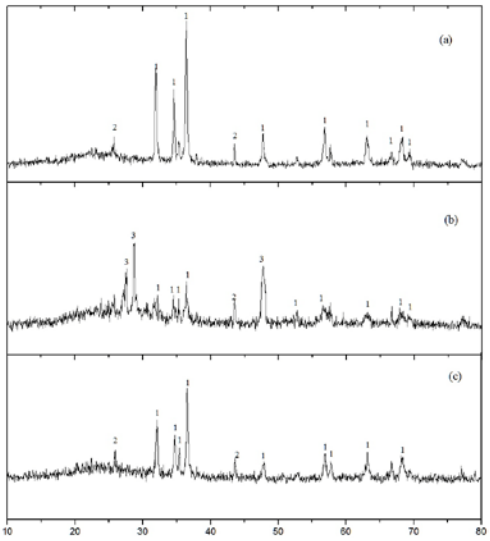

Figure 1: XRD patterns of (a) calcined (at 1073 K for 2 h), (b) sulfurized with 1% H_2S/N_2 (873 K), and (c) regenerated with air (873 K) ZnO/CF. (1: ZnO; 2: SiO_2; 3: ZnS).

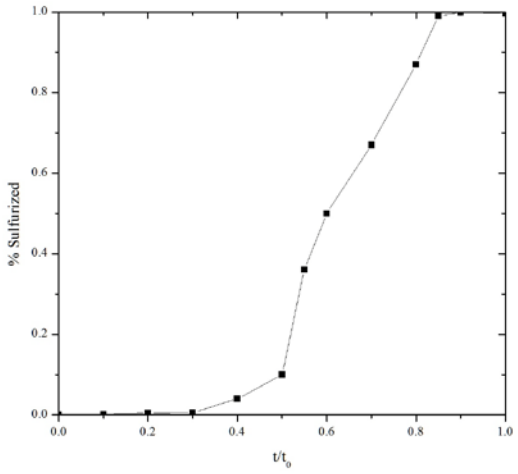

Figure 2: Time dependence desulfurization of a simulated gas containing 1% of H_2S with ZnO/CF at 873 K.

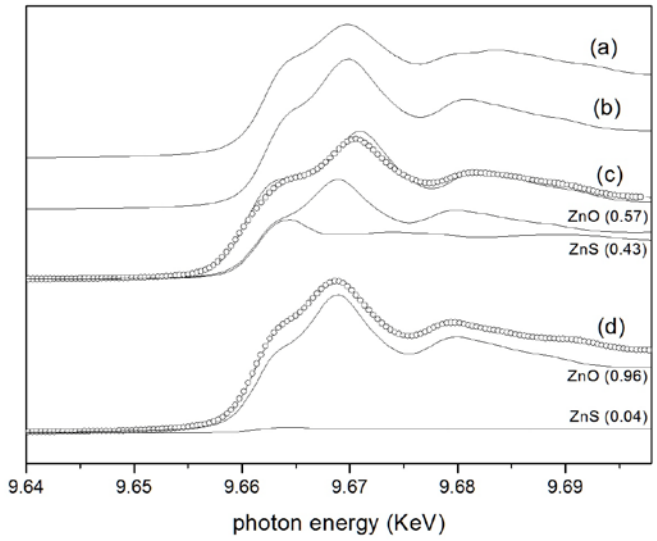

Figure 3: Component fitted XANES spectra of zinc in (a) nano ZnO and (b) oxidized (at 1073 K), (c) sulfurized (at 873 K) and (d) regenerated ZnO/CF (at 873 K).

ACKNOWLEDGEMENT

The financial supports of the Taiwan National Science Council, Bureau of Energy, and National Synchrotron Radiation Research Center are gratefully acknowledged.

REFERENCES

[1] A. Giuffrida, M. C. Romano, and G. G. Lozza, Applied Energy, 87, 3374-3383, 2010.
[2] M. Pérez-Fortes, A. D. Bojarski, E. Velo, J. M. Nougués, and L. Puigjaner, Energy, 34, 1721-1732, 2009.
[3] R. Clift and J. P. K. Seville, Eds., 1993.
[4] D. Koch, W. Cheung, J. P. K. Seville, and R. Clift, Filtration & Separation, 29, 337-341, 1992.
[5] A. M. Robin, Ed. Blackie Academic & Professional, 1993.
[6] J. Seville, T. G. Chuah, V. Sibanda, and P. Knight, Advanced Powder Technology, 14, 657-672, 2003.
[7] J. Stringer, Powder Technology, 80, 275-276, 1994.
[8] S. D. Sharma, M. Dolan, D. Park, L. Morpeth, A. Ilyushechkin, K. McLennan, D. J. Harris, and K. V. Thambimuthu, Powder Technology, 180, 115-121, 2008.
[9] K. V. Thambimuthu, IEA Coal Research, 1993.
[10] J. R. Grace, Powder Technology, 93, 89-91, 1997.
[11] I. Rosso, C. Galletti, M. Bizzi, G. Saracco, and V. Specchia, Industrial & Engineering Chemistry Research, 42, 1688-1697, 2003.
[12] E. A. Stern, M. Newville, B. Ravel, Y. Yacoby, and D. Haskel, Physica B, 208-209, 117-120, 1995.
[13] S. I. Zabinsky, J. J. Rehr, A. Ankudinov, R. C. Albers, and M. J. Eller, Physical Review B, 52, 2995-3009, 1995.