High-temperature Desulfurization with Nanosize ZnO


*Department of Environmental Engineering, National Cheng Kung University, Tainan 701, Taiwan, wanghp@mail.ncku.edu.tw
**Department of Safety, Health and Environmental Engineering, National Kaohsiung First University of Science & Technology, Kaohsiung 811, Taiwan, george@ccms.nkfust.edu.tw
***Department of Environmental Science and Engineering, Tunghai University, Taichung 407, Taiwan, yulin@thu.edu.tw

ABSTRACT

Thermal efficiencies of an integrated gasification combined cycle (IGCC) process can be enhanced with high-temperature desulfurization. Nanosize, sub-nano (clusters) and atomic-dispersed ZnO were prepared for the high-temperature desulfurization. An enhanced absorbance of the nanosize ZnO at 9668 eV is found by X-ray absorption near edge structure (XANES) spectroscopy. ZnO clusters are also observed in the channels of MCM-41. By temperature programmed sulfurization (TPS) and oxidization (TPO), it is found that the nanosize ZnO can be effectively sulfurized and regenerated (with air) at 940-950 K. The smaller ZnO clusters in MCM-41 can be sulfurized at relatively lower temperatures (700-820 K). The atomic dispersed ZnO on TiO₂ having the strong metal-support interactions cannot be sulfurized at the temperatures of <960 K, and interestingly a small amount of ZnS can be regenerated at much lower temperatures (i.e., <650 K). It seems that the nano- or sub-nano-(cluster)-size dispersed ZnO may be desired for the high-temperature desulfurization especially for a high efficiency IGCC based electric power generation process.

Keywords: desulfurization, nanosize ZnO, XANES, EXAFS

1 INTRODUCTION

High temperature gas desulfurization is an important process for the removal of hydrogen sulfide from hot flue gas in the integrated gasification combined cycle (IGCC) power plants. Zinc based sorbents are effective for reducing H₂S [1]. ZnO has been known very effective in desulfurization and regeneration. However, ZnO may also be reduced to yield metallic zinc (Zn) in the reducing environment during desulfurization at elevated temperatures. Two possible methods for reduction of Zn evaporation at high temperatures are: (1) reduced the ZnO size to nano scales and (2) chemically modified ZnO. In order to improve the H₂S removal efficiency, metal compounds such as TiO₂ were frequently added in the ZnO matrix [2].

MCM-41 (mesoporous composite material) with the structure of an array of tubular channels (in diameters of 1.5-10 nm) has attracted great attention due to its high thermal stability at the temperature of 1300 K and high porosity and surface areas (500-1500 m²/g). Therefore, MCM-41 is frequently used as supports for H₂S sorbents [3]. ZnO may be incorporated in MCM-41 to increase the contact area and mechanical strength [4-9].

X-ray absorption spectroscopy can be used to observe chemical structure of select metals or metal oxides in complex matrixes. Intensity of the synchrotron radiation X-ray is over 1000 times than normal one. For instance, X-ray can penetrate into catalysts and monitor their electronic and local structure of the catalytically active centers. X-ray absorption near edge structure (XANES) spectroscopy is very useful in determination of elements with a different environment and degree of aggregation or location [10-15]. Thus the main objective of this work was to study speciation of nanosize ZnO and ZnO clusters in the channels of MCM-41 as well as ZnO supported on TiO₂ by XANES spectroscopy.

2 EXPERIMENTAL

To prepare MCM-41, a mixture containing sodium silicate solution (14% of NaOH, and 27% of SiO₂) (Fisher Scientific), fumed silica (Sigma), cetyltrimethylammonium bromide (CTMABr) gel and tetramethylammonium hydroxide (TMAOH) (Lancaster) was stirred well at 298 K for 2 h. The molar ratio of the main components in the mixture was SiO₂ : TMAOH : CTMABr : H₂O = 1.0 : 0.27 : 0.58 : 86. A diluted sulfuric acid solution was used to adjust the pH values of the mixture solution between 11 and 12. The mixture was then heated in a teflon lined autoclave (100 mL) at 423 K for 48 h. The as-synthesized MCM-41 was stirred well at 298 K for 2 h. The molar ratio of the main components in the mixture was SiO₂ : TMAOH : CTMABr : H₂O = 1.0 : 0.27 : 0.58 : 86. A diluted sulfuric acid solution was used to adjust the pH values of the mixture solution between 11 and 12. The mixture was then heated in a teflon lined autoclave (100 mL) at 423 K for 48 h. The as-synthesized MCM-41 was filtered, washed with deionized water, dried at 378 K for 16 h and calcined at 823 K for 10 h. The ZnO/MCM-41 and ZnO/TiO₂ desulfurization absorbents were prepared by impregnation of an aqueous solution containing 0.1 M Zn(NO₃)₂ onto the MCM-41 and TiO₂, respectively. The absorbents were dried at 378 K for 16 h and calcined at 823 K for 2 h.
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 GeV (ring current = 120-200 mA). A Si(111) double-crystal monochromator was used for selection of energy. The energy resolution (ΔE/E) of the beamline 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.

In the temperature programmed sulfurization (TPS) (TGA TA SDT-Q600) experiments, temperatures were raised from 373 to 1073 K under 100 mL/min of 3% H2S/N2 at a heating rate of 5 K/min. For regeneration of the sulfurized absorbents, temperature programmed oxidation (TPO) was conducted with a 100 mL/min flowing air. During TPO or TPS, off gases was monitored by FTIR (Biorad, FTS-40).

3 RESULTS AND DISCUSSION

XANES can provide molecular scale data of oxidation states of excited atoms, coordination geometry and bonding of local environment in complex matrix. Generally, the size of the ZnO clusters is limited to the openings (<4 nm in diameters) of MCM-41. The XANES spectra in Fig. 1 show a shoulder at 9669 eV which can be attributed to the 1s-to-3d transition of Zn(II). An enhanced absorbance at 9668 and 9664 eV (white line) indicates the existence of nanosize ZnO. The XANES spectrum of the ZnO/TiO2 shows an enhanced absorbance at 9665 eV which indicates the formation of zinc titanates.

At the preparation and calcinations conditions of the ZnO/TiO2, Zn may react with TiO2 and form zinc titanates in the forms of Zn2TiO4, ZnTiO3 or Zn2Ti3O8 [2, 16]. The sulfurized ZnO/TiO2 contains 36% of ZnS and 64% of ZnO. In the calcined ZnO/MCM-41, the major zinc species are nanosize ZnO (75%) and Zn2SiO4 (25%). At the temperature of 823 K, ZnO interacts with the amorphous SiO2 in the wall of MCM-41 and leads to the formation of Zn2SiO4. 25% of ZnS and 75% of ZnO are found in the sulfurized ZnO/MCM-41.

Figure 2 shows the TPS and TPO of bulky and nanosize ZnO, ZnO/TiO2 and ZnO/MCM-41. During sulfurization, an increase of 20% of ZnS is found. The maximum sulfurization rate for nanosize ZnO is found at 873 K, which is less than that of the bulk ZnO by about 70 K. As expected, the nanosize ZnO can be sulfurized and regenerated at a lower temperature than the bulk ZnO because the surface atoms in nanoparticles have fewer nearest neighbors and are more weakly bound and less constrained and consequently less energy is needed.

On the contrary, a higher sulfurization temperature (>960 K) for ZnO/TiO2 is needed, which is possibly because of the effect of strong metal-support interaction (SMSI) in the ZnO/TiO2. The ZnS/TiO2 can be regenerated at much lower temperatures than the bulky ZnO. A small amount of ZnS is oxidized at the temperature of <650 K, suggesting that the ZnO/TiO2 can be better used for high temperature desulfurization and regeneration.
ZnO clusters in MCM-41 is sulfurized at temperatures of 703 and 823 K as H_2S molecules (<0.6 nm) can freely diffuse into the channels of MCM-41 (4 nm). However, ZnS in the channels of MCM-41 can be regenerated at a higher temperature (920-1030 K) which may be due to the strong interactions between ZnS and MCM-41.

The ZnO/TiO_2 has high removal efficiencies of hydrogen sulfide [17, 18] and is found to be reduced more slowly to volatile Zn than the bulky ZnO [19]. It is very likely that TiO_2 can retard the reduction of ZnO to volatile Zn in the high temperature sulfurization process and prevent the loss of the ZnO/TiO_2 [2, 18].

4 CONCLUSION

XANES spectra show that a small amount of zinc reacts with TiO_2 and SiO_2 in the ZnO/TiO_2 and ZnO/MCM-41, respectively in the sulfurization process. When sulfurized, 36% and 25% of ZnS are found in ZnO/TiO_2 and ZnO/MCM-41, respectively. As expected, nanosize ZnO can be sulfurized and regenerated at the temperatures less than bulky ZnO. The ZnO/TiO_2 chemically affected by SMSI can be sulfurized at >960 K and regenerated at <650 K. The ZnO/MCM-41 can be sulfurized at <823 K and regenerated at >920 K, suggesting that less energy is required for the sulfurization of ZnO/MCM-41, however, additional energy is needed for the regeneration process.

ACKNOWLEDGMENT

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

REFERENCES