FULL LENGTH ARTICLE

Immobilization of elemental mercury in non-ferrous metal smelting gas using ZnSe$_{1-x}$S$_x$ nanoparticles

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GRAPHICAL ABSTRACT

ARTICLE INFO

Keywords:
Elemental mercury
Selenium
Zinc sulfide
Non-ferrous smelting gas
Sulfur dioxide

ABSTRACT

Gaseous elemental mercury (Hg$^0$) in non-ferrous smelting gas is generally accompanied by a high concentration of SO$_2$. Traditional sorbents for Hg$^0$ removal often suffer from SO$_2$ poisoning. To develop a sorbent that has high mercury removal efficiency and excellent sulfur resistance, Zn-Se-S composites were selected. The experimental results indicated that the ZnSe$_{0.7}$S$_{0.3}$ composite had the best Hg$^0$ removal performance, achieving an Hg$^0$ removal efficiency higher than 99% after 120 min of reaction at 150 °C. A "hump" was observed in the adsorption breakthrough curve. This phenomenon is due to the activation of surface Se$^0$, with reduction in surface oxidation state (from Se$^{2+}$ to Se$^0$) by Hg$^0$ or SO$_2$. This composite has multiple adsorption sites (Se$^0$ and active S) for mercury uptake from smelting gas. Moreover, this specific Zn-Se-S composite had excellent SO$_2$ resistance. Even high concentrations (1000 or 2000 ppm) of SO$_2$ barely influenced Hg$^0$ removal performances. The Zn-Se-S composite exhibited potential for Hg$^0$ removal from non-ferrous smelting gas.

https://doi.org/10.1016/j.fuel.2019.115641

Received 22 March 2019; Received in revised form 27 May 2019; Accepted 11 June 2019
Available online 15 June 2019

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1. Introduction

Mercury is a hazardous element in the environment owing to its high toxicity, long persistence, and bioaccumulation ability [1,2]. The Minamata Convention on Mercury, a global treaty aimed at controlling mercury from primary emission sources and replacing mercury products such as mercurial thermometers and fluorescent lamps, was approved by 128 countries on August 16, 2017 [3]. China has always been considered the country with the highest mercury emissions. Mercury emissions from coal-fired power plants and non-ferrous metal smelting plants are two primary anthropogenic sources [4–6]. Nowadays, most of the mercury emitted from coal-fired power plants can be efficiently captured using current devices, such as electrostatic precipitators/fabric filter precipitators (ESP/FF), selective catalytic reduction (SCR) units, and wet flue gas desulfurization (WFGD) equipment [7–9]. However, there are no suitable technologies for mercury removal from non-ferrous smelting gas.

Among various non-ferrous metal smelting processes, zinc production is a typical one [10–12]. The general process for Zn production and waste disposal is illustrated in Fig. S1. Hg and Zn elements are sulfophile elements and often exist as HgS and ZnS, respectively, in ores. After smelting in the roaster, mercury will be emitted from the ores at high temperature and exist as gaseous elemental mercury (Hg0) in the smelting gas. In addition, the associated sulfur in ores will be converted to SO2. High concentrations of SO2 and Hg0 coexist in the smelting gas, forming S-Hg mixed smelting gas. In general, mercury and SO2 in the smelting gas can get the level of 10 mg·m−3 and 4–5%, respectively [13,14]. High concentration of SO2 is used to produce sulfuric acid (H2SO4) after purification system. With decreasing temperature, part of the Hg0 can transform to oxidized mercury (Hg2+) via reaction with some oxidative components. Part of the Hg2+ will be converted to small particulate mercury (Hg0) in the smelting gas. Hg0 can be captured in dust removal devices. Hg2+ can be captured by scrubbers due to its solubility, and dissolved Hg2+ in washing liquid could result in the generation of waste acid that contains mercury. It is difficult to dispose of such wastewater. However, it cannot be efficiently captured using scrubbing towers owing to the high volatility and insolubility of Hg0. According to our test results at the zinc smelter, the Hg0 removal efficiency of the scrubbing process and electrostatic demister is 18% and 5%, respectively [15,16]. Hg2+ can be oxidized to oxo-mercury (HgOx2−) via reaction with some oxidants [17].

To evaluate the Hg0 removal efficiency, a fixed-bed adsorption system was assembled. A schematic diagram of the experimental system is shown in Fig. S1. Mercury emissions from non-ferrous smelting gas. High mercury capacity.

Sulfur minerals with abundant reduced sulfur species, which has a strong affinity with mercury. Yang et al. used magnetic pyrrhotite (Fe1−xS) to remove Hg0 [33]. The experimental results indicated that Fe1−xS has a gaseous Hg0 removal rate of 0.28 μg·(g·min)−1 at 60 °C and a Hg0 adsorption capacity of 0.22 mg·g−1. Li et al. synthesized nano-ZnS particles for Hg0 removal [34]. The nano-ZnS was superior in both Hg0 adsorption capacity and reaction rate. Some novel sulfide chalcogens were also selected for gaseous mercury removal [35].

In this study, a series of Se-modified ZnS nanoparticles were synthesized, and their mercury capture performance were investigated in simulated flue gas. The optimal reaction temperature and the influence of flue gas components on Hg0 removal efficiency were studied. The Hg0 removal mechanism was also analyzed based on the experimental and characterization results. The ultimate aim is to develop an effective sorbent which is suitable for industrial application in Hg0 removal from non-ferrous smelting flue gas.

2. Experimental section

2.1. Preparation of materials

Preparation of ZnSe1−xSx nanoparticles: In a typical procedure, Zn(NO3)2 was first dissolved in 100 mL of ethanol. Then, Se powder and Na2S solution were added and the mixture was heated at 100 °C for 2 h. The molar ratio of Zn(Se + S) was 1:1. The mixture was transferred into a 200 mL. Teflon-lined stainless-steel autoclave. The autoclave was sealed and heated at 120 °C for 12 h, followed by cooling to ambient temperature. The obtained product was thoroughly washed with ethanol and filtered several times and to remove the unreacted nitrates. For comparison, pure ZnS and ZnSe were also synthesized using the same method.

2.2. Characterization of materials

The Powder X-ray diffraction (XRD) patterns were determined by a Shimadzu XRD-6100 diffractometer with Cu Kα radiation at room temperature. The data were recorded at a step of 10°·min−1 in the range of 10–80°. The surface composition was determined by X-ray photoelectron spectroscopy (XPS). The results were recorded with a XPS instrument (Ultra DLD, Shimadzu-Kratos) with Al Kα as the excitation source, and the binding energy was calibrated using the C 1s line at 284.6 eV.

2.3. Measurement of gaseous mercury adsorption performance

To evaluate the Hg0 removal efficiencies of the as-prepared materials, a lab-scale fixed-bed adsorption system was assembled. A schematic of this process is shown in the Supporting Information (Fig. S1). This evaluation system contained a feed gas system, gaseous Hg0 generator, quartz reactor, Hg0 detection system, and tail-gas purification system. In general, O2, gaseous Hg0, and SO2 vapor were distributed using pure N2. To provide a constant gaseous Hg0 (about 1.0 mg·m−3), a Hg0 permeation device was placed in an unchanged temperature (43 °C)
oil bath. The total flow rate was maintained as 500 mL/min with a mass flow controller. For each experiment, 25 mg of prepared samples was placed into a quartz tube with an inner diameter of 5 mm. The off-gas coming from reactor passed through an active carbon and KMnO₄ solution the exhaust gas cleaning. The reaction temperatures were controlled from 50 to 150 °C by temperature control devices. Before each test, the simulated flue gas contained Hg⁰ was firstly bypassed the sorbent bed and passed into the Hg⁰ detection system until the inlet Hg⁰ concentration was stable. The inlet and outlet Hg⁰ concentrations were detected by a cold-vapor atomic absorption spectrometer (CVAAS) mercury detector, which was calibrated via a Lumex RA 915+. The time for each test was 2 h. The Hg⁰ removal efficiencies were calculated according to Eq. (1):

\[
\text{Hg⁰ removal efficiency} = \frac{\text{Hg}_{\text{in}}^0 - \text{Hg}_{\text{out}}^0}{\text{Hg}_{\text{in}}^0}
\]

where \(\text{Hg}_{\text{in}}^0\) is the inlet concentration of Hg⁰, and \(\text{Hg}_{\text{out}}^0\) is the outlet concentration of Hg⁰.

3. Results and discussion

3.1. Hg⁰ removal performance

3.1.1. Hg⁰ removal performance of various materials

The Hg⁰ removal performance of as-prepared samples is shown in Fig. 1. ZnS, ZnSe, and ZnSe₁₋ₓSₓ composites (of different ratios) were tested for comparison under 5% O₂ atmosphere at 100 °C. ZnS nanoparticles had high Hg⁰ removal performance (Hg⁰ removal efficiency of almost 100%) during the first 20 min of the reaction. However, after 100 min of reaction, the Hg⁰ removal efficiency dropped sharply, to only approximately 50%. For the ZnSe composite, the initial removal efficiency was much lower than that of ZnS. However, the Hg⁰ removal efficiency gradually increased after the first several minutes. The curve exhibited a "hump" shape. The same phenomenon appeared in the curves of the other ZnSe₁₋ₓSₓ samples, especially ZnSe₀.₅S₀.₅. Although ZnSe₀.₅S₀.₅ had the lowest Hg⁰ removal efficiency, the Hg⁰ removal efficiency gradually increased after the first 5 min. Among the ZnSe₁₋ₓSₓ samples, ZnSe₀.₅S₀.₅ had the highest Hg⁰ removal efficiency, approximately 85%, which was maintained throughout the reaction. It was speculated that some of this composite's active sites were activated when it reacted with gaseous Hg⁰. For comparison, the Hg⁰ adsorption capacity of other sorbents reported in the literatures were summarized in Table S2 [34,40–42].

3.1.2. Effect of temperature on Hg⁰ removal performance

Temperature is an important factor for gaseous reactions and it determines the applicability of different sorbents for treatment of real smelting gas. In a typical non-ferrous smelting plant, the flue gas temperature at upstream unit of ESP in a zinc production plant is about 250 °C, and the temperature reduced to 30–100 °C after scrubbing towers. The effects of temperature on Hg⁰ removal efficiency by ZnSe₀.₇S₀.₃, ZnSe₀.₅S₀.₅, and ZnSe₀.₅S₀.₁ are shown in Fig. 2(a). This reaction exhibited some obvious "hump" curves under various reaction temperatures. When the temperature was lower than 100 °C, the Hg⁰ removal efficiencies were approximately 80%. At a temperature of 100 °C, the Hg⁰ removal efficiency was about 90% after 120 min of reaction. As the reaction temperature increased, the Hg⁰ removal efficiencies further increased. When the reaction temperature was 125 °C, the Hg⁰ removal efficiency was nearly 100%. The same phenomenon (higher Hg⁰ removal efficiency) was observed at 150 °C. When the temperature was higher than 150 °C, the Hg⁰ removal efficiencies were higher than that of lower temperatures (< 150 °C). However, the composite was decomposed when the temperature was higher than 150 °C. As shown in Fig. 2(b), the red part at the end of the reaction tube indicates the decomposition products of Se⁰. The Zn-Se-S composite was destroyed at such high temperatures [39]. Therefore, the Zn-Se-S composite can only be used at lower temperatures below 150 °C. Moreover, capturing Hg⁰ at this temperature can avoid gaseous Hg⁰ entering the scrubber system and producing waste acid, which is more difficult to treat.

3.1.3. Effect of SO₂ on Hg⁰ removal performance

Obviously, Zn-Se-S composites can be applied at lower temperatures. They can be used upstream of scrubbing towers in a zinc production plant. In this unit, SO₂ was the primary gas component and could reach thousands-ppm level. Usually, SO₂ has a poisonous effect on Hg⁰ removal for various kinds of sorbents [20,43]. The effects of SO₂ on Hg⁰ removal by ZnSe₀.₇S₀.₃ were investigated, and the results are shown in Fig. 3(a). The total Hg⁰ removal efficiencies were calculated based on the 120 min reaction. When 1000 ppm SO₂ was added to the simulated smelting gas, the Hg⁰ removal efficiencies were higher than 90%, whether at 75 °C, 100 °C, or 125 °C. Similarly, when 2000 ppm SO₂ was added to the simulated gas, SO₂ barely inactivated Hg⁰ removal efficiencies. To further investigate the effect of SO₂, the ZnSe₀.₅S₀.₅ composite was first pretreated with 1000 ppm or 2000 ppm SO₂ for 2 h. Then, the composites were tested for Hg⁰ removal at 100 °C. The results are shown in Fig. 3(b). The Hg⁰ removal efficiencies of the pre-sulfurized composites were higher than 90%, even in the first several minutes. These results further indicated that this composite has excellent resistance to SO₂.

3.2. Hg⁰ removal mechanism of the Zn-Se-S composite

3.2.1. Physical structure characterization

The X-ray diffraction patterns of the ZnSe₁₋ₓSₓ samples are presented in Fig. 4. For ZnSe, all diffraction peaks in the XRD patterns belong to crystalline ZnSe and no diffraction peaks of elemental Zn, Se, and S or other components were observed [44]. For ZnS, the XRD peaks corresponded to the standard values for ZnS [45]. For the composites of Zn-Se-S, Se-rich samples mainly presented the structure of ZnSe, whereas S-rich samples primarily presented the structure of ZnS. For ZnSe₀.₇S₀.₃, it is obvious that the crystal structures of ZnSe and ZnS coexisted. Furthermore, with the addition of Se to ZnS, a porous structure and larger surface area were the results.

3.2.2. Surface chemical analysis

To further investigate the surface composition before and after the reaction, XPS analysis was performed. The spectra for XPS analysis are shown in Fig. 5, and the analysis data are shown in Table S1. As shown in Fig. 5(a), for ZnS, the two peaks centered at 162.9 and 161.7 eV were assigned to surface active sulfur and S⁰, respectively [36]. For the
ZnSe_{0.7}S_{0.3} composite sample, two peaks at 163.1 and 161.8 eV were also assigned to active S and S^{2−}, respectively [34,46]. However, the constitution of these two sulfur species varied. Active S represented 45.35% and 17.48% of the sulfur in ZnS and the ZnSe_{0.7}S_{0.3} composite, respectively. The Se 3d spectra are shown in Fig. 5(b). For ZnSe, the spin orbit splitting of the 3d states was divided into 3d 5/2 and 3d 3/2 states. The observed binding energy of Se 3d 5/2 and Se 3d 3/2 was at 55.1 and 56.0 eV, respectively, which was attributed to Se. For the ZnSe_{0.7}S_{0.3} composite, the peak at 55.3 eV was associated with Se^0 and the broad peak near 58.9 eV indicated the surface oxidation state of Se [47]. Furthermore, the peak at 54.4 eV was assigned to ZnSe in the composite.

After the reaction, the spent composites were also analyzed. As shown in Fig. 5(c), after reaction with Hg^0, for S 2p, two peaks, at 163.2 and 161.9 eV, were assigned to active S and S^{2−}, respectively. However, the ratio of active S to the total sulfur changed after the reaction, increasing from 17.48% of the fresh sample to 21.30% of the spent sample. After the reaction of SO_2 + Hg^0, the peaks' positions were the same as those for the fresh sample. The proportion of active S was further increased to 24.17%. During the reaction, the active S increased on the surface of the composite. As shown in Fig. 5(d), for Se 3d, after reaction with Hg^0, only two peaks, at 59.3 and 54.8 eV, were detected. The peak at 59.3 eV was assigned to the surface oxidation states of Se. And a wide peak was generated from 52–57 eV, indicating that part of high valence of Se was reduced to the low valence state. In addition, part of Se can combine with the Hg^0 and form HgSe after adsorption. Se^2− can also combine with Hg^{2+} and form HgSe. It is difficult to distinguish these different binding peak due to the similar binding energies. Therefore, we only can see a wide peak based on the XPS results. The same phenomenon can be seen in the spectrum after the reaction of SO_2 + Hg^0, where only two peaks appeared, which are assigned to the surface oxidation states of Se and the low valence state of Se. In addition, the ratio of Se oxidation state to the total Se dropped from 34.96% in the after Hg^0 reaction sample to 29.07%. This could be the result of the reduction effect of SO_2. Obviously, Se changed significantly during the reaction with Hg^0. Moreover, for the spectra of Hg 4f, as shown in Fig. 5(e), when reacted with Hg^0, two peaks, at 104 and 100.0 eV, were assigned to Hg 4f 5/2 and Hg 4f 7/2, respectively [34,46].

Based on the above discussion and as shown in Fig. 6, the Hg^0 removal mechanism can be described as follows. First, gaseous Hg^0 was adsorbed onto the surface of the composite, the larger surface area of
which benefits this physical adsorption process, thus adsorbed mercury (≡Hg0) was formed. Second, the ≡Hg0 reacted with Se (≡Se2-) and transformed to ≡Hg2+ along with the reduction of ≡Se2+ to ≡Se0. The chemistry of mercury and selenium, particularly the readily interactive electron orbitals of elemental selenium, predisposes its binding to elemental mercury with high affinity [48]. Then, the surface ≡Hg0 reacted with ≡Se0 and formed ≡Hg-Se. Herein, we can find the “hump effect,” which refers to the activation of surface ≡Se0. In addition, the surface active S (=S) which contains S and S2− also reacted with ≡Hg or ≡Hg2+ and formed surface ≡HgS. The reactions illustrating these processes are as follows:

\[
\text{Hg}_0 + \text{Se}_0 \rightarrow \text{HgSe} \tag{2}
\]

\[
\equiv \text{Hg}_0 + \equiv \text{Se}^2+ \rightarrow \equiv \text{Hg}^2+ + \equiv \text{Se}_0 \tag{3}
\]

\[
\equiv \text{Se}_0 + \equiv \text{Hg}_0 \rightarrow \equiv \text{Hg} + \text{Se} \tag{4}
\]

\[
\equiv \text{S} (\equiv S^-) + \equiv \text{Hg} (\equiv \text{Hg}^2+/\equiv \text{Hg}) \rightarrow 2 \equiv \text{HgS} \tag{5}
\]

Furthermore, this composite had excellent SO2 resistance. On one hand, pure Se and surface-active S could not react with SO2, which protected the composite. On the other hand, SO2 could react with ≡Se2+ to form ≡Se0, the surface ≡Se0 can react with ≡Hg0 and form HgSe.

Therefore, Zn-Se-S exhibited a higher Hg0 removal efficiency as well as excellent SO2 resistance. Such composites have two types of active sites for mercury capture. Se0 can capture surface Hg0 and form HgSe. Surface active S can capture surface Hg2+ and form HgS. In addition,
SO2 and Hg0 can promote the transformation of surface Se2+ to Se6, thereby enhancing Hg0 removal performance. These characteristics make Zn-Se-S composites promising materials for mercury uptake from a S-Hg mixed flue gas.

4. Conclusion

In this work, the Zn-Se-S ternary composites were synthesized to capture Hg0 from non-ferrous smelting gas. The Zn-Se-S exhibit higher mercury removal efficiency and excellent SO2 resistance compared with that of ZnS and ZnSe. And ZnSe0.7S0.3 composite had the best Hg0 capture performance, achieving an Hg0 removal efficiency higher than 99% after 120 min at 150 °C. A “hump” effect was observed in the adsorption breakthrough curve, which is due to the activation of surface Se6, with reduction in surface oxidation state (from Se2+ to Se0) by Hg0 or SO2. The multiple adsorption sites (Se6 and active S) attributed to excellent Hg0 adsorption capacity from smelting gas, where Hg0 was immobilized as HgS and HgSe on the Zn-Se-S surface. The ZnSe0.7S0.3 can be used upstream of scrubbing towers for mercury uptake, making Zn-Se-S exhibit higher mercury removal efficiency at 150 °C. Moreover, the addition of 1000 or 2000 ppm SO2 had a slight effect on Hg0 removal efficiency, indicating an excellent SO2 resistance. These results demonstrated the Zn-Se-S can be used upstream of scrubbing towers for mercury uptake, indicating promising material for removing Hg0 from non-ferrous smelting gas.

Acknowledgements

This study was supported by the National Key R&D Program of China (2017YFC0210500) and the National Natural Science Foundation of China (No. 21860105 and No. 51578354). This study was also supported by the National Postdoctoral Program for Innovative Talents (No. BX201700151). We are grateful for the support of China’s Post-doctoral Science Fund (No. 2017M620156).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2019.115641.

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