Research Article

Characteristics and Stability of Mercury Vapor Adsorption over Two Kinds of Modified Semicoke

Zhang Huawei, Liu Xiuli, Wang Li, and Liang Peng

College of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao, Shandong Province 266510, China

Correspondence should be addressed to Zhang Huawei; sdlkdzhw@163.com

Received 20 June 2014; Accepted 5 August 2014; Published 27 August 2014

Academic Editor: Wenjun Jiang

Copyright © 2014 Zhang Huawei et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In an attempt to produce effective and lower price gaseous Hg\textsuperscript{0} adsorbents, two methods of HCl and KMnO\textsubscript{4}/heat treatment were used respectively for the surface modification of lignite semicoke from Inner Mongolia. The different effects of modification process on the surface physical and chemical properties were analyzed. The characteristics and stability of mercury vapor adsorption over two kinds of modified semicoke were investigated. The results indicated that modification process caused lower micropore quantity and volume capacity of semicoke; the C-Cl functional groups, C=O bond and delocalized electron \(\pi\) on the surface of Cl-SC, the amorphous higher valency Mn\(^{\text{\textsuperscript{2+}}}\), and O=C–OH functional groups on the surface of Mn-H-SC were the active sites for oxidation and adsorption of gaseous Hg\textsuperscript{0}. Modification process led to higher mercury removal efficiency of semicoke at 140\(\degree\)C and reduced the stability of adsorbed mercury of semicoke in simulated water circumstance simultaneously.

1. Introduction

Gaseous Hg\textsuperscript{0} pollutant in flue gas has the properties of being stable, thermodynamic, and insoluble in water, and its removal techniques have become a research focus. At present, one of the most effective ways for gaseous Hg\textsuperscript{0} removal is injecting varieties of solid adsorbents into flue gas, which can oxidize the elemental mercury into Hg\textsuperscript{2+} and capture it [1]. Previous research shows that high efficiency gaseous Hg\textsuperscript{0} adsorbents can be prepared using cheap porous materials by physical and chemical surface modification methods [2–6]. Lignite semicoke has similar chemical properties with activated carbon, but its price is only one-third of activated carbon or so, which can be widely used as low-cost adsorbent in the fields of flue gas desulfurization and denitrification, oil purification, and wastewater treatment [7–9]. However, there are seldom reports about semicoke as mercury adsorbents of flue gas; the well-developed pore structure and abundant functional groups on the surface of semicoke can provide active sites for the removal of gaseous Hg\textsuperscript{0} [10]. It is expected to prepare high efficiency and cheap gaseous Hg\textsuperscript{0} adsorbents by surface modification of lignite semicoke.

For the mercury adsorbed semicoke, it must be disposed as dangerous goods due to its high mercury content and potential toxicity; therefore, the mercury stability on the surface of adsorption product is the major factor which determines its subsequent treatment process. Indeed, in most of coal-fired power plants, the adsorbents injection device is always installed in the upstream of dust cleaning equipment, and the semicoke after mercury adsorption reaction would be captured together with fly ash in the dust cleaning unit. Fly ash is a kind of precious resource and can be used for the preparation of glass ceramics, cement, fertilizer, and sewage purification material [11, 12]. If the adsorbed mercury on the surface of semicoke is not stable, it will pollute the fly ash product. In the subsequent process of fly ash utilization, the adsorbed mercury is likely to reescape due to the influence of environmental temperature, humidity, and solution pH value and thus causes secondary pollution on the environment. Therefore, it is necessary to investigate the adsorbed mercury speciation and stability on the semicoke surface and provide reference data for follow-up treatment measure and process for the adsorption product.

2. Experimental

2.1. Sample Preparation. The lignite semicoke used in the tests is from the Huolin River of Inner Mongolia; the
preparation method is as follows: we placed a coal sample in a 700°C muffle furnace, conducted 1 h of destructive distillation under anoxic conditions, cooled it to room temperature, and then smashed it to 80 to 100 meshes for use and recorded it as NM-SC; we soaked 10 g of prepared NM-SC for 24 h into mass fractions 25% HCl solution, with a 1:3 of solid-liquid ratio; after the reactions were completed, we filtrated and dried the sample, and the semicoke treated with 1:3 of solid-liquid ratio; after the reactions were completed, we filtrated and dried the sample, and the semicoke treated

2.2. Characterization. The physical characterizations of the samples were analyzed by the Brunauer-Emmett-Teller (BET) method, and the surface area and pore size distribution were obtained by adsorbing and desorbing in N\textsubscript{2} at 77 K, using an automatic volumetric multipoint apparatus (SSA-4300). Before the measurements were taken, all of the samples were outgassed at 100°C for 2 h. The microstructures of the samples were characterized by scanning electron microscopy (KYKY2800B). X-ray photoelectron spectroscopy (Thermo ESCALAB250) with Al K\textalpha (hv = 1486.6 eV) as the excitation source was used to determine the binding energies of C1s, O1s, Mn2p, and Hg4f. The C1s line at 284.6 eV was taken as a reference for the binding energy calibration.

2.3. Mercury Adsorption Experimental Methodology and Instrumentation. A small fixed bed reactor described in [4] was employed to evaluate the gaseous Hg\textsuperscript{0} removal efficiency of semicoke under the simulated flue gas condition. The adsorption efficiency was calculated as follows:

\[ \eta = 1 - \frac{C_t}{C_0}, \]

where \( \eta \) indicates adsorption efficiency, \( C_0 \) is the initial concentration of gaseous Hg\textsuperscript{0}, and \( C_t \) indicates the concentration of gaseous Hg\textsuperscript{0} after adsorption. The mercury volume quantity in unit mass of adsorbent was calculated as follows:

\[ q = \frac{C_0 L t - \int_0^t C L dt}{m}, \]

where \( q \) represents mercury volume quantity in unit mass of adsorbent, \( L \) is the gas flow, \( t \) is the adsorption time, and \( m \) is the dosage of adsorbent.

Mercury concentration in flue gas was measured online by QM201 mercury analyzer, in which detection range is from 0 to 50 \( \mu \)g/m\textsuperscript{3}, and mercury concentration in leaching solution was measured by SG-921 mercury analyzer, in which detection range is from 0.1 to 10 ng/mL.

2.4. The Toxicity Characteristic Leaching Procedure and Sequential Chemical Extraction Experiments of Adsorption Products. The toxicity characteristic leaching procedure (TCLP) tests are carried out according to the methods in [13]; we weighed 0.5 g adsorption sample accurately, put it in glacial acetic acid solution whose pH value is 4.93, where the mass ratio of solid to liquid is 1:20, impregnated it for 20 h, and determined the mercury concentration in the supernatant. The details of sequential chemical extraction experiments are given in [14,15]; the semicoke samples of adsorption products were extracted using the following solutions: (1) 1 mol/L MgCl\textsubscript{2}, (2) 10 mol/L HCl, (3) 2 mol/L HNO\textsubscript{3}, (4) 50 g/L Na\textsubscript{2}S in 10 g/L NaOH, and (5) aqua regia. The corresponding mercury forms in extraction for each step are as follows: (1) water soluble, (2) exchangeable, (3) hydrochloric acid soluble, (4) nitric acid soluble, and (5) mercuric sulfide and residual mercury.

3. Results and Discussion

3.1. Analysis of Specific Surface Area and Pore Structure. From the data shown in Table 1, the specific surface area and pore structure analysis of three kinds of semicoke, it can be seen that the surface area and total pore volume were slightly increased after HCl treatment; this is because HCl can react with ash in semicoke and produce soluble chloride; part of channels blocked by ash are got through in the following washing process and cause the surface area and total pore volume to increase. However, the HCl treatment only increased the volumes of the mesopores and macropores; in the meantime, it also gave rise to the partial transition of the micropores to mesopores and macropores; this conclusion is consistent with previous research of Dubinin [16] and Yanxu et al. [17]. After K\textsubscript{2}MnO\textsubscript{4}/heat treatment, the specific surface area of semicoke decreased, the proportion and volume of micropores obviously reduced, and the average pore size increased, which indicated that part of micropore structures were destroyed during the K\textsubscript{2}MnO\textsubscript{4}/heat treatment process.

3.2. Analysis of Scanning Electron Microscopy (SEM). Figure 1 describes the surface microtopography of NM-SC, CI-SC, and Mn-H-SC. It can be seen that the surface of crude semicoke is flat, and the pores on the sample have

| Sample     | BET surface area (m\textsuperscript{2}/g) | Average pore size (nm) | Total Pore volume (m\textsuperscript{3}/g) | Proportion % |
|------------|------------------------------------------|-------------------------|-------------------------------------------|--------------|
|            |                                          |                         | Total Micro (≤2 nm)                       |              |
| NM-SC      | 84.203                                   | 2.55                    | 0.107                                     | 72.4         |
| CI-SC      | 97.278                                   | 2.96                    | 0.113                                     | 62.3         |
| Mn-H-SC    | 65.494                                   | 3.67                    | 0.120                                     | 50.2         |

Table 1: The BET surface area and pore parameters of semicoke.
the properties of uneven size and irregular shape. HCl treatment did not destroy the pore structure of crude semicoke but clearly generated many new pores with different sizes. After KMnO$_4$/heat treatment, the surface of Mn-H-SC was covered by a layer of attachment; parts of pores were blocked up and caused the surface roughness of the samples to increase significantly.

### 3.3. Analysis of X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was applied to analyze the surface oxygenic functional groups of three kinds of adsorbents (NM-SC, Cl-SC, and Mn-H-SC), two kinds of adsorbents with captured gaseous Hg$^0$ (Hg-Cl-SC and Hg-Mn-H-SC), and valence state of manganese oxide of two samples (Mn-H-SC and Hg-Mn-H-SC). The narrow region spectrum of C$_1$s and Mn$_{2p}^{3/2}$ was fitted by multipeaks using XPS Peak Processing software. The fitting parameters of C$_1$s are C–C (284.0–285.1 eV), C–OR (285.3–287.0 eV), C=O (286.8–288.1 eV), and O=C–OH (288.1–290.0 eV) [18], and those of Mn$_{2p}^{3/2}$ are Mn$^{7+}$ (645.6 eV), Mn$^{6+}$ (644.2 eV), Mn$^{4+}$ (643.0 eV), Mn$^{3+}$ (642.1 eV), and Mn$^{2+}$ (641.0 eV) [19, 20].

According to the fitting results of C$_1$s spectrum shown in Table 2, it may be concluded that C–C carbon species are the main carbon components on the surface of SC (51.37%), followed by the carbon species C–OR (34.32%), C=O (9.48%), and O=C–OH (4.83%). HCl modification increased the carbon species of C–C, C=O, and O=C–OH by 15.59%, 1.74%, and 4.20%, respectively, and reduced the carbon species of C–OR by 21.53%. After KMnO$_4$/heat treatment, the carbon species of C–C and C=O decreased by 23.80% and 2.04%, respectively, and reduced the carbon species of C–OR by 21.53%. After KMnO$_4$/heat treatment, the carbon species of C–C and O=C–OH on semicoke increased by 23.80% and 2.04% and C–OR and C=O decreased by 20.92% and 4.92%, respectively. In general, two kinds of modification methods can increase graphitization degree, the content of carboxylic acid and ester chemical functional groups of semicoke. HCl treatment also increased the content of alcohols, ethers, ketones, quinones,
Table 3: Distribution of surface Mn ions of Mn-H-SC, and Hg-Mn-H-SC.

| Sample    | Mn$^{7+}$ (%) | Mn$^{6+}$ (%) | Mn$^{4+}$ (%) | Mn$^{3+}$ (%) | Mn$^{2+}$ (%) | Mn AOS |
|-----------|---------------|---------------|---------------|---------------|---------------|--------|
| Mn-H-SC   | 0.00          | 10.62         | 35.59         | 32.57         | 21.22         | 3.46   |
| Hg-Mn-H-SC| 0.00          | 0.00          | 32.02         | 44.10         | 23.88         | 3.08   |

AOS: average oxidation state.

and other chemical functional groups, and K$_2$MnO$_4$/heat treatment reduced the content of those functional groups. For CI-SC and Mn-H-SC samples, surface graphite carbon content increased slightly after gaseous Hg$^0$ adsorption, while the carbon content of carbonyl or quinone functional groups and carboxyl or ester functional groups decreased slightly; it is probably due to the fact that, in the gaseous Hg$^0$ adsorption process, part of C=O groups of ketones, quinones, carboxylic acids, and esters oxidized gaseous Hg$^0$ and at the same time it was reduced, causing the C=O double bond to be broken, thus resulting in the decrease of carbonyl or quinone functional groups and carboxyl or ester functional groups of semi coke.

The Mn$^{2p_{3/2}}$ multi peak fitting results of Mn-H-SC and its adsorption product are shown in Table 3. It can be seen that the average oxidation degree of manganese on the surface of Mn-SC is 3.46; there is no Mn$^{7+}$ compounds. These results indicated that the potassium permanganate decomposed during the modification, and a portion was reduced to a lower valence state by the surface organic functional groups or carbon atoms of semi coke [21, 22]. After gaseous Hg$^0$ adsorption at 140°C, compared with Mn-H-SC, the average manganese oxidation state on Hg-Mn-H-SC surface reduced by 0.38, Mn$^{7+}$ spectrum peak disappeared, the atomic ratio of Mn$^{4+}$ decreased slightly, and the atomic ratio of Mn$^{3+}$ and Mn$^{2+}$ rose sharply. This showed that Mn$^{4+}$ and Mn$^{3+}$ on the surface of Mn-H-SC would oxidize gaseous Hg$^0$ to Hg$^{2+}$ in adsorption process and were reduced to their lower valence state, Mn$^{3+}$ and Mn$^{2+}$.

3.4. Gaseous Hg$^0$ Adsorption Characteristics of Semi coke.

In Figure 2, under the conditions that the inlet mercury concentration is 30 µg/m$^3$, gas flow is 1 L/min, adsorbent is 0.50 g, and adsorbent temperature is 30°C and 140°C, the gaseous Hg$^0$ removal efficiency of NM-SC, CI-SC, and Mn-H-SC is described in Figure 2.

It is observed that when the adsorption temperature is 30°C, NM-SC has a good mercury removal performance. At low temperature, gaseous Hg$^0$ takes physical adsorption as the primary reaction on the semi coke surface; the gaseous Hg$^0$ is primarily absorbed in the micropores, and the surface area and pore structure of semi coke are the principal factors that determine the mercury removal performance. The analysis data of the specific surface area and pore structure showed that the crude semi coke had a relatively large specific surface area and pore volume, and the surface micropore proportion reached to 72.4%; the average pore diameter was 2.55 nm; thus it has high mercury removal efficiency. The BET analysis data showed that although HCl treatment increased the total pore volume and surface area of semi coke slightly, the proportion and volume of micropore declined and the physical adsorption capacity of semi coke to gaseous Hg$^0$ reduced to a certain extent, thereby leading to CI-SC that presented lower mercury removal efficiency. K$_2$MnO$_4$/heat
treatment decreased mercury removal efficiency of semicoke at 30°C obviously; it is due to the fact that a portion of pores on semicoke surface is clogged by attachments after modification process, and heat treatment at 260°C causes partial collapse of micropores, which led to part transition of micropores to mesopores, so the micropore portion and volume of Mn-H-SC were significantly lower than NM-SC and performed poor mercury removal performance at 30°C.

When the adsorption temperature is 140°C, the mercury removal efficiency of CI-SC was much higher than that of NM-SC and was maintained above 90% after 140 min adsorption reaction. Gaseous Hg\(^{0}\) mainly takes chemical adsorption on semicoke surface at high temperature; HCl treatment has great influence on surface chemical properties of semicoke, mainly to increase the contents of the functional groups such as carboxyl and the phenolic hydroxyl groups, and in the modification process, the Cl\(^-\) in hydrochloric acid solution can take ion-exchange reaction on the semicoke surface, thus enabling part of chlorine elements to be absorbed on the semicoke surface and forming the Cl-C-Cl functional groups. When the concentration of the Cl\(^-\) on the semicoke surface is high, the gaseous Hg\(^{2+}\) can react with Cl\(^-\) and produce mercury chlorides, such as [HgCl\(^{+}\)], HgCl\(_2\), or [HgCl\(_2\)]\(^{2-}\) [23, 24]. The C=O bond and delocalized electron \(\pi\) on the semicoke surface also may be taken as electron acceptors, thus enabling the reaction between Hg\(^{2+}\) and Cl\(^-\) to be conducted towards the positive direction and generating the stable chloride of mercury. Both the oxygen-containing functional groups and chlorine-containing groups on CI-SC surface can provide active sites for gaseous Hg\(^{2+}\) oxidation and chemical adsorption, thus remarkably increasing the mercury removal efficiency of CI-SC at 140°C. The mercury removal efficiency of Mn-H-SC was slightly lower than CI-SC but significantly higher than NM-SC. KMnO\(_4\)/heat treatment modification can increase the content of O=C-OH groups in carboxyl and ester groups on semicoke surface and generate the amorphous MnO\(_x\) compounds with higher valence; the average oxidation degree of manganese is 3.46. Gaseous Hg\(^{2+}\) can be oxidized to Hg\(^{2+}\) by high valence Mn\(^{2+}\) and O=C-OH functional groups and chemically adsorbed in the pore channels of Mn-H-SC, making the mercury removal performance improve significantly.

3.5. Mercury Speciation and Stability on the Surface of Semicoke. For adsorption products, the adsorbed mercury stability in simulated water environment was investigated using TCLP leaching tests, and the mercury speciation on the surface of semicoke was studied using sequential chemical extraction experiments.

The TCLP leaching experiment results of three kinds of semicoke samples are shown in Table 4. It can be seen from the TCLP tests data that the mercury stability of semicoke samples after adsorption reaction has great relationship on the adsorption temperatures and modification methods of semicoke. For the samples of 30°C mercury adsorption products, no mercury was detected in the leachate of NM-SC samples; mercury concentrations in the leachate of CI-SC and Mn-H-SC were 7.6 \(\mu\)g/L and 9.0 \(\mu\)g/L, respectively, which are lower than the safe concentration of TCLP standard value of 25 \(\mu\)g/L. The stability of adsorbed mercury in micropores of semicoke is relativity better at low temperatures and is not easy to escape in the leaching process. The micropore proportion of CI-SC and Mn-H-SC samples is lower than that of NM-SC, so causing the mercury stability on the surface of semicoke to somewhat decrease. For the samples of 140°C mercury adsorption products, the mercury concentration in the filtrate of CI-SC sample was the highest and reached 168.2 \(\mu\)g/L; the mercury concentration in the filtrate of Mn-H-SC sample was higher than that of NM-SC. At higher adsorption temperature, gaseous Hg\(^0\) can be oxidized to HgCl\(_2\) and HgO, respectively, on the surface of CI-SC and Mn-H-SC. The solubility of elemental mercury, HgO, and HgCl\(_2\) is 0.06, 53, and 6.9 \(\times\) \(10^4\) mg/L, respectively; HgCl\(_2\) is easily soluble in water, which makes the mercury concentration in the filtrate of CI-SC sample significantly high; HgO has lower solubility in water, so the mercury concentration in the filtrate of Mn-H-SC sample is below the safety standard value. In short, the modification process improved the mercury removal performance of semicoke at high temperatures but in different extent reduced the stability of adsorbed mercury on the surface of semicoke in simulated water environment.

The sequential chemical extraction experiment results for semicoke adsorption products are shown in Table 5. The experiment error of total mercury content is less than 10%, which indicated the reliability of the sequential chemical extraction. In the sequential extraction process, the extract of the first step is water soluble mercury; the exchangeable mercury of the second step mainly refers to the organic mercury which is instable on the surface of semicoke; the hydrochloric acid dissolved mercury of the third step means the HgO generated by the reaction of gaseous Hg\(^0\) and active oxidation in semicoke such as manganese oxides MnO\(_x\) and amorphous and crystalline Fe, Al oxides; the nitrate dissolved mercury of the fourth step refers to the elemental mercury adsorbed on the semicoke surface; the extract of the fifth and sixth steps is HgS and residual mercury, respectively [15, 25]. For the mercury adsorption products of NM-SC, CI-SC, and Mn-H-SC at 30°C and 140°C, the content of HgS and residual mercury was about 10%, which may be HgS partially contained in semicoke itself or the stable forms of mercury generated in the reaction of gaseous Hg\(^0\) and sulfur or nitrogen element in semicoke.

Water soluble and exchangeable mercury were not detected in the extract of NM-SC adsorption product at 30°C, and 2.8% of hydrochloric acid solution mercury were detected, which is the HgO generated in the reaction of gaseous Hg\(^0\) and oxygen-containing functional groups or the amorphous and crystalline Fe, Al oxides in semicoke; the

| Sample     | NM-SC | CI-SC | Mn-H-SC |
|------------|-------|-------|---------|
| 30°C       | 0.18  | 7.6   | 168.2   |
| 140°C      | 9.0   | 3.3   |         |

BDL: below detection limitation.
Table 5: Sequential extraction procedure results of semicoke adsorption products.

| Sample | Water soluble (%) | Exchangeable (%) | HCl soluble (%) | HNO₃ soluble (%) | HgS (%) | Residual (%) | Total (%) |
|--------|------------------|-----------------|----------------|-----------------|---------|-------------|-----------|
| NM-SC  |                  |                 |                |                 |         |             |           |
| 30°C   | 0                | 0               | 2.8            | 86.9            | 3.2     | 5.7         | 98.6      |
| 140°C  | 0                | 1.1             | 24.9           | 61.6            | 5.3     | 4.9         | 97.8      |
| Cl-SC  |                  |                 |                |                 |         |             |           |
| 30°C   | 0.9              | 2.6             | 6.5            | 79.7            | 4.8     | 3.9         | 98.4      |
| 140°C  | 64.4             | 13.2            | 15.1           | 2.7             | 3.6     | 3.3         | 102.3     |
| Mn-H-SC|                  |                 |                |                 |         |             |           |
| 30°C   | 0                | 1.7             | 5.9            | 79.1            | 5.4     | 4.3         | 96.4      |
| 140°C  | 3.8              | 6.4             | 67.2           | 15.3            | 5.1     | 4.8         | 102.6     |

Content of nitrate soluble mercury is as high as 89.6%, which is mainly the elemental mercury physical adsorbed on the semicoke surface. For the extract of NM-SC adsorption product at 140°C, hydrochloric acid soluble mercury content increased to 24.9% and nitric acid soluble mercury content reduced to 61.6%, indicating that the content of HgO increased, while the content of elemental mercury decreased in the sample of NM-SC adsorption product at high temperatures.

It could detect 79.7% of elemental mercury in the extract of Cl-SC adsorption product at 30°C and also contained a small amount of oxidation states and unstable organic mercury. For the adsorption product of 140°C, mercury mainly exists in water soluble form, and its content is 64.4%; this is because the gaseous Hg⁰ can take reaction with Cl element of semicoke and generate HgCl₂ with high solubility. There was also part of exchangeable and acid soluble mercury on Cl-SC, mainly referring to unstable organic mercury or HgO generated in the reaction of gaseous Hg⁰ with surface oxygen-containing groups such as carboxyl, lactone, and hydroxyl.

The main mercury form of Mn-H-SC adsorption products at 30°C and 140°C was elemental and HgO, respectively.

4. Conclusions

(1) Hydrochloric acid treatment mainly increased the volume of mesopores and macropores of semicoke and the content of chemical functional groups such as alcohols, ethers, ketones, and quinines on the semicoke surface. KMnO₄/heat treatment combination modification process caused a decrease of micropore proportion on the semicoke surface, increased the graphitization degree and the content of carboxylic acid or ester chemical functional groups, and reduced the chemical functional groups content of alcohols, ethers, ketones, and quinines.

(2) Gaseous Hg⁰ mainly took physical adsorption on the surface of semicoke at low temperature, while chemical adsorption was the main mechanism at high temperature; the Cl–C–Cl functional groups, C=O bonds and delocalized electrons π of Cl-SC, and the high valence Mn⁰⁺ and O=C–OH functional groups of Mn-H-SC could be taken as electron acceptors, made gaseous Hg⁰ oxidize to Hg²⁺, and chemically adsorbed in the pore channel of semicoke, thus improving the mercury removal efficiency of semicoke obviously.

(3) The TCLP leaching experiment results indicated that the modification process could improve the mercury removal performance of semicoke at high temperatures but in different extent reduced the stability of adsorbed mercury on the surface of semicoke in simulated water environment. The contents of elemental mercury were the highest in three samples after 30°C adsorption, and the major adsorbed mercury forms of NM-SC, Mn-H-SC, and Cl-SC after 140°C adsorption were elemental HgO and HgCl₂, respectively.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This study was supported by the National Natural Science Foundation of China (nos. 21060659 and 21276416), the Foundation of State Key Laboratory of Mining Disaster Prevention and Control Cofounded by Shandong Province and the Ministry of Science and Technology, and the Graduate Science and Technology Innovation Fund (YCI40215).

References

[1] H. Yang, Z. Xu, M. Fan, A. E. Bland, and R. R. Judkins, “Adsorbents for capturing mercury in coal-fired boiler flue gas,” *Journal of Hazardous Materials*, vol. 146, no. 1-2, pp. 1–11, 2007.
[2] S. H. Lee, Y. J. Rhim, S. P. Cho, and J. I. Baek, “Carbon-based novel sorbent for removing gas-phase mercury,” *Fuel*, vol. 85, no. 2, pp. 219–226, 2006.
[3] P. Zhao, X. Guo, and C. Zheng, “Removal of elemental mercury by iodine-modified rice husk ash sorbents,” *Journal of Environmental Sciences*, vol. 22, no. 10, pp. 1629–1636, 2010.
[4] H. Zhang, J. Chen, P. Liang, and L. Wang, “Mercury oxidation and adsorption characteristics of potassium permanganate modified lignite semi-coke,” *Journal of Environmental Sciences*, vol. 24, no. 12, pp. 2083–2090, 2012.
[5] Y. Wang and Y. Duan, “Effect of manganese ions on the structure of Ca(OH)\textsubscript{2} and mercury adsorption performance of Mn\textsuperscript{2+}/Ca(OH)\textsubscript{2} composites,” Energy and Fuels, vol. 25, no. 4, pp. 1533–1538, 2011.

[6] J. M. Gatica and H. Vidal, “Non-cordierite clay-based structured materials for environmental applications,” Journal of Hazardous Materials, vol. 181, no. 1–3, pp. 9–18, 2010.

[7] X. R. Zheng, W. R. Bao, Q. M. Jin et al., “Impact of impregnation pressure on desulfurization performance of Zn-based sorbents on semi-coke,” Journal of Natural Gas Chemistry, vol. 21, no. 1, pp. 56–60, 2012.

[8] J. P. Wang, Z. Yan, L. L. Liu et al., “Low-temperature SCR of NO with NH\textsubscript{3} over activated semi-coke composite-supported rare earth oxides,” Applied Surface Science, vol. 309, no. 1, pp. 1–10, 2014.

[9] P. Parastoo, A. Alla, K. Kambiz et al., “Removal of organic compounds and trace metals from oil sands process-affected water using zero valent iron enhanced by petroleum coke,” Journal of Environmental Management, vol. 139, no. 15, pp. 50–58, 2014.

[10] W. H. Zhang, X. Liu L, and L. Wang, “Mercury adsorption form and stability on the surface of lignite semi-coke,” Journal of China Coal Society, vol. 39, no. 4, pp. 776–781, 2014.

[11] Y. Zhao, J. Zhang, C. Tian, H. Li, X. Shao, and C. Zheng, “Mineralogy and chemical composition of high-calcium fly ashes and density fractions from a coal-fired power plant in China,” Energy and Fuels, vol. 24, no. 2, pp. 834–843, 2010.

[12] C. Cao, T. Peng, and W. Ding, “Effect of crystallization temperature on crystallization and properties of CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}-Fe\textsubscript{2}O\textsubscript{3} glass ceramics from coal fly ash,”Journal of the Chinese Ceramic Society, vol. 41, no. 1, pp. 122–128, 2013.

[13] Z. Luo, C. Hu, J. Zhou, and K. Cen, “Stability of mercury on three activated carbon sorbents,” Fuel Processing Technology, vol. 87, no. 8, pp. 679–685, 2006.

[14] J. W. Graydon, X. Zhang, D. W. Kirk, and C. Q. Jia, “Sorption and stability of mercury on activated carbon for emission control,” Journal of Hazardous Materials, vol. 168, no. 2–3, pp. 978–982, 2009.

[15] C. Sladek and M. S. Gustin, “Evaluation of sequential and selective extraction methods for determination of mercury speciation and mobility in mine waste,” Applied Geochemistry, vol. 18, no. 4, pp. 567–576, 2003.

[16] M. M. Dubinin, “Fundamentals of the theory of adsorption in micropores of carbon adsorbents: characteristics of their adsorption properties and microporous structures,” Carbon, vol. 27, no. 3, pp. 457–467, 1989.

[17] L. Yanxu, C. Jiangyao, and S. Yinghuang, “Adsorption of multicomponent volatile organic compounds on semi-coke,” Carbon, vol. 46, no. 6, pp. 858–863, 2008.

[18] U. Zielke, K. J. Hüttinger, and W. P. Hoffman, “Surface-oxidized carbon fibers: I. Surface structure and chemistry,” Carbon, vol. 34, no. 8, pp. 983–998, 1996.

[19] M. Oku, “X-ray photoelectron spectra of KMnO\textsubscript{4} and K\textsubscript{2}MnO\textsubscript{4} fractured in situ,” Journal of Electron Spectroscopy and Related Phenomena, vol. 74, no. 2, pp. 135–148, 1995.

[20] I. M. Neshit and D. Banerjee, “Interpretation of XPS Mn(2p) spectra of Mn oxyhydroxides and constraints on the mechanism of MnO\textsubscript{2} precipitation,” American Mineralogist, vol. 83, no. 3–4, pp. 305–315, 1998.

[21] S. Dash, S. Patel, and B. K. Mishra, “Oxidation by permanganate: synthetic and mechanistic aspects,” Tetrahedron, vol. 65, no. 4, pp. 707–739, 2009.