Removal of Mercury from Simulated Natural Gas by SO2 Activated Petroleum Coke

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Abstract. A preparation method based on the carbon-thermal reduction reaction was proposed to make petroleum coke-based mercury adsorbent. The effects of activation agent flow rate, time and inlet mercury concentration on mercury removal were investigated. Mercury adsorption experiments were carried out on a fixed-bed reactor system under simulated natural gas atmosphere. Meanwhile, the mercury removal mechanism was put forward based on the characterization results, including surface area and micropore structure, element contents and active chemical functional groups. The results show that the raw petroleum coke (RPC) has almost no mercury removal capacity while the mercury removal efficiency of the sulfur activated petroleum coke (SPC) is greatly improved. After activation, specific surface area and micropores increased significantly. The sulfur content increased as well. Meanwhile, the relative content of non-oxidative sulfur forms and oxygen functional groups of SPC are significantly higher than RPC. The optimum parameters of activation agent flow rate and time of 100 mL/min and 1.5 h are reached in this experiment, respectively.

Keywords. High-sulfur petroleum coke, SO2 activation, mercury adsorption, simulated natural gas.

1. Introduction

As a clean energy source, natural gas exhausts far less pollutants than coal and oil. In recent years, the production proportion of natural gas in the world’s energy structure has been continuing to grow, and it is expected to approach that of coal by 2035 [1]. However, mercury, a kind of trace substance with hypertoxic, atmospheric mobility, persistence and bioaccumulation, is ubiquitous in fossil fuel resources such as natural gas, and its concentration ranges generally 1-200 μg·m⁻³ [2-3]. In natural gas liquefaction, elemental mercury not only corrodes aluminium heat exchanger, but also threatens the safety of operators [4-5]. Therefore, it is of great significance to remove elemental mercury in natural gas for the safe surrounding of work. Among many of techniques of mercury removal from natural gas, the chemical adsorption by using sulfur-loaded activated carbon is known as a common and effective way for industrially handling high volume rate of natural gas supply [3, 6].

In view of the dual pressure of economy development and environmental protection, more and more researchers are committed to the reuse of industrial and agricultural waste to prepare adsorbents with high mercury removal performance. As a by-product of the refining process, petroleum coke, which is
an ideal raw material for preparation of activated carbon, has the advantages of high carbon content, low volatile content, abundant raw materials and low price. Therefore, to find an economic and effective way to fabricate sulfur-loaded activated carbon from petroleum coke is an effective way to make the resource recycling utilization. It is a promising way to use the carbon-thermal reduction reaction to prepare the sulfur-loaded petroleum coke as a mercury adsorbent by SO$_2$ activation modification at high temperature that features both physical pore expansion and chemical sulfur-loading. The overall carbon-thermal reduction reaction is as follows [7]: 

\[
\text{SO}_2 + C \rightarrow \text{CO}_2 + \frac{1}{2} \text{S}_2
\]

According to some researches [8-10], the gas-phase mercury can react with the sulfur on the surface of the adsorbent in the form of HgS, resulting in improved pore structures and abundant sulfur-containing functional groups on surface of SO$_2$ activated petroleum coke.

In this paper, the effects of activation agent flow rate, activation time and inlet mercury concentration on mercury removal performance were studied. The mercury adsorption performance was investigated on a fixed-bed reactor system under simulated natural gas atmosphere. Meanwhile, the mercury removal mechanism was put forward by characterization methods, including surface area and porosity analyser, elemental analyser and X-ray photoelectron spectroscopy (XPS).

2. Experimental Method

2.1. Sample Preparation

In this experiment, a kind of high sulfur petroleum coke (RPC, Raw Petroleum Coke) was selected as the raw material, and its ultimate analysis is shown in table 1.

| Sample | C (%) | H (%) | O (%) | N (%) | S (%) |
|--------|-------|-------|-------|-------|-------|
| RPC    | 88.73 | 2.571 | 1.04  | 1.31  | 6.233 |

The preparation of sulfur-loaded petroleum coke is as follows: after RPC being crushed and sieved, the particles within 100-200 mesh in diameter are dried to a designated weight in oven at 105 °C; 5 g of raw petroleum coke is evenly laid in a 15 mm inner diameter quartz tube which is placed in a horizontal tube furnace; a certain amount of activation agent flow of 20% SO$_2$ passes through the quartz tube at 700 °C which is heated at a constant heating rate; after RPC was activated for a certain time, the heating stops and the SO$_2$ gas is cut off to obtain the sulfur-loaded petroleum coke (SPC). The samples are named as SPC-x-y, in which x and y represents the activation flow rate (mL/min) and activation time (h), respectively.

2.2. Experimental Apparatus and Procedure

The mercury adsorption experiments of sulfur-loaded petroleum coke were carried out on a fixed-bed reactor system as shown in figure 1.

In the experiment, the high-purity CH$_4$ was taken as the simulated natural gas. Partial CH$_4$, as the carrier gas to carry a constant concentration of mercury into the system that occurred through a permeation tube (VICI METRONICS, America) sealed in a U-shaped borosilicate glass tube, premixed with a certain amount of balanced CH$_4$ in a premixing chamber. Then it passed through the fixed-bed reactor and reacted with samples (RPC and SPC). The Lumex-RA-915 (LUMEX INSTRUMENTS, Russia) on-line mercury analyser monitored the mercury concentration of the outlet gas, and then the exhaust gas was discharged after purification by activated carbon.

2.3. Evaluation of Mercury Removal Performance

The mercury removal performance of the sample was evaluated by Hg$^0$ breakthrough rate $\eta$ (%):
Figure 1. Fixed-bed reactor system.

$$\eta = \frac{C_{\text{out}}}{C_{\text{in}}} \times 100\%$$

where $C_{\text{in}}$ and $C_{\text{out}}$ represent Hg concentration of the inlet and outlet of the fixed bed experimental device, respectively, $\mu g \cdot m^{-3}$, mercury removal rate is $1-\eta$.

3. Results and Discussion

3.1. Specific Surface Area and Elemental Analysis

Figure 2 shows the $N_2$ adsorption/desorption isotherm curves of RPC and SPC. It can be seen that the $N_2$ adsorption/desorption curve of RPC has no obvious inflection point under low pressure. According to IUPAC’s classification [11], it belongs to type III adsorption/desorption isotherm curve. After being activated by SO$_2$, adsorption curve type changed to type I. At low relative pressure, the isotherm shows a large and steep rise, and then bend into a platform, reflecting the micropore filling phenomenon of microporous adsorbent.

Table 2 lists the results of pore structure parameters and elemental analysis of RPC/SPC. The results show that RPC is densely structured and has no developed pore structure. After SO$_2$ activation, the pore structure is obviously improved, the micropore and total pore volume are significantly increased. Firstly, the water and volatile matters inside the petroleum coke vaporise, which leave a lot of pores [12]. Besides, the release of CO$_2$ and S$_2$ vapor generated by the carbon-thermal reduction reaction from the surface and inside of the petroleum coke, consuming a part of carbon, thereby forming rich pore structure.

Figure 2. $N_2$ adsorption/desorption isotherms of RPC/SPC.
Table 2. Pore structure parameters and elemental analysis of RPC/SPC.

| Sample | \( S_{\text{BE}} \) (m\(^2\)·g\(^{-1}\)) | \( V_{\text{micro}} \) (cm\(^3\)·g\(^{-1}\)) | \( V_{\text{total}} \) (cm\(^3\)·g\(^{-1}\)) | \( V_{\text{micro}} / V_{\text{total}} \) (%) | \( d_{\text{pore}} \) (nm) | C (%) | H (%) | N (%) | S (%) |
|--------|-------------------------------|---------------------------------|---------------------------------|---------------------------------|----------------|-----|-----|-----|-----|
| RPC    | 2.099                         | 0.0074744                       | 0                               | 14.243                         | 88.73          | 2.571 | 1.31 | 6.233 |
| SPC    | 58.233                        | 0.0251                          | 0.028416                        | 1.952                          | 79.70          | 1.995 | 0.99 | 11.222 |

3.2. XPS Analysis

The surface properties and sulfur forms of petroleum coke adsorbents have a great influence on mercury removal performance. Therefore, the surface property of activated petroleum coke was characterized by XPS. In this experiment, elemental sulfur is scarcely present in RPC since it will escape into the gas phase in the form of sulfur vapor. The spectra of \( S_2p \) and \( C_{1s} \) of petroleum coke before and after activation and the results of peak fitting are shown in figure 3. Table 3 gives the relative content of sulfur forms and oxygen functional groups of RPC/SPC.

![Figure 3. XPS spectra of \( S_2p \) and \( C_{1s} \) of RPC/SPC.](image)

Table 3. Sulfur forms and oxygen functional groups of RPC/SPC.

| Sample | R-S | Sth/S\(^0\) | R-SO | R-SO\(_2\) | SO\(_4^{2-}\) | Non-oxidative sulfur | C-O | C=O | COOH/ C(O)- O-C | Oxygen functional groups |
|--------|-----|------------|------|------------|-----------|----------------------|-----|-----|----------------|--------------------------|
| RPC    | 0   | 96.71      | 0    | 0          | 3.29      | 0                    | 33.77 | 0   | 33.77         |                          |
| SPC    | 3.79| 80.97      | 7.46 | 4.47       | 3.32      | 11.25                | 41.58 | 6.83| 3.60          | 52.01                    |

It was found that the surface sulfur forms of the RPC mainly exists in the form of thiophene (Sth) and sulfate (SO\(_4^{2-}\)), and the relative content of thiophene is as high as 96.7%. After SO\(_2\) modification, the sulfur form mainly exists in the form of sulphide (R-S), thiophene, sulfoxide (R-SO), sulfone (R-SO\(_2\)) and sulfate. Sth is a structurally stable cyclic sulfur with weaker binding ability to Hg\(^0\). While R-S and R-SO belong to non-oxidative sulfur, non-oxidative sulfur has an unpaired lone pair of electrons,
which can interact with Hg$_0$ to form a covalent bond, or as an initial point of attachment to achieve oxidative removal of Hg$_0$ [8]. What is more, SPC has more abundant oxygen functional groups compared with RPC, and the newly added carbonyl and ester functional groups can promote the removal of elemental mercury [13-14].

3.3. Mercury Adsorption Characteristics

3.3.1. Effects of SO$_2$ Activation on Mercury Removal. Figure 4 shows the Hg$_0$ breakthrough rate curves of RPC and SPC when the inlet mercury concentration is 110 μg•m$^{-3}$ and the adsorption temperature is 50 °C. It can be seen that RPC has almost no mercury removal capacity. The physical adsorption of RPC is weak because of its dense structure and undeveloped structure. In addition, from the results of XPS, the number of oxygen-functional groups is small. Although the sulfur content reaches 6.233%, it is mainly composed of Sth and SO$_4^{2-}$. As a result, mercury removal performance of RPC is poor. On the contrary, mercury removal performance after activation enhanced greatly. There are two possible reasons. Firstly, the pore structure is enriched. Secondly, sulfur content, non-oxidative sulfur forms and oxygen functional groups which are beneficial for Hg$_0$ adsorption together increased significantly.

![Figure 4. Effect of SO$_2$ activation on mercury breakthrough rate.](image)

3.3.2. Effects of Activation Time on Mercury Removal. Figure 5 shows the mercury breakthrough rate curves of SPC of different activation time when the inlet mercury concentration is 110 μg•m$^{-3}$ and the adsorption temperature is 50 °C. As can be seen from figure 5., the sample SPC-100-1.5 has the best mercury removal performance. When activation time is too short, SO$_2$ and carbon can not be reacted completely. When the activation time increases, pore structure becomes more developed, which contributes to the enhancement of physical adsorption. Moreover, carbon-thermal reaction becomes fully completed, resulting in more sulfur content and surface functional groups. However, the long activation time at 700 °C could damage the pore structure of the sample. But it has little impact as we can see in that the curve of activation time of 1.5 h and 2 h is very close.

![Figure 5. Effect of activation time on mercury breakthrough rate.](image)
3.3.3. Effects of Activation Flow Rate on Mercury Removal. Figure 6 shows the mercury breakthrough rate curves of SPC of different activation flow rate when the inlet mercury concentration is 110 μg·m⁻³ and the adsorption temperature is 50 °C. Since pre-mixed SO₂ is used here, the amount of SO₂ directly affects mercury adsorption performance by affecting the pore structure and sulfur content of the sample. As the amount of SO₂ increases, mercury adsorption efficiency has been greatly improved and it reached the best at 100 mL/min. When the flow rate continues to increase, excess SO₂ overreacted with carbon to damage the original pore structure.

![Figure 6. Effect of activation flow rate on mercury breakthrough rate.](image)

3.3.4. Effects of Inlet Mercury Concentration on Mercury Removal. Figure 7 shows the mercury breakthrough rate curves obtained by mercury adsorption with the sample SPC-100-1 and adsorption temperature of 50 °C. It can be seen that removal efficiency of mercury is lower with the increase of mercury concentration. This may be because that the amount of adsorbent is relatively small (100mg) in the experiment [15], while the mercury-contained simulated gas flow rate used may be too much to be reacted by the adsorbent, resulting the extra elemental mercury passing away directly through the adsorption layer before being adsorbed. Thus, when the mercury concentration in natural gas and flow rate is higher, the amount of adsorbent should be higher accordingly to achieve the desired mercury adsorption efficiency.

![Figure 7. Effect of inlet mercury concentration on mercury breakthrough rate.](image)

4. Conclusions
A preparation method based on the carbon-thermal reduction reaction was proposed to make petroleum coke-based mercury adsorbent. The effects of activation agent flow rate, time and inlet mercury concentration on mercury removal were investigated. The mercury removal mechanism was put forward based on the characterization results. The following conclusions were reached:

(1) Raw petroleum coke has almost no mercury removal capacity. After activation and modification by SO₂, the mercury removal efficiency of sulfur-loaded petroleum coke is improved a lot.
(2) After SO\textsubscript{2} activation, specific surface area and micropores of the raw petroleum coke increased significantly with the sulfur content increment as well. The relative content of the active non-oxidative sulfur forms and oxygen functional groups of SPC is significantly higher than RPC.

(3) The optimum parameters of activation agent flow rate and time in this experiment are 100 mL/min and 1.5 h, respectively. High inlet mercury concentration will reduce mercury removal efficiency. The amount of adsorbent has to match that of the mercury-contained natural gas flow rate.

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