Effects of CO and CO\textsubscript{2} on the Removal of Elemental Mercury over Carbonaceous Surfaces

Qixin Zhou, Jinsong Zhou,\textsuperscript{*} Hui Cao, and Xinyu Xu

Cite This: ACS Omega 2021, 6, 2916–2924

ABSTRACT: Coal gasification is a popular method for the optimization of coal utilization and the reduction of environmental pollutant emissions. However, the reductive atmosphere of its products is disadvantageous for removing elemental mercury (Hg\textsuperscript{0}). Activated cokes (AC) was employed in this work for mercury capture in a reducing atmosphere. The high-temperature heating decreases the mercury-removal capability of carbon sorbents because the carbonaceous surface is becoming oxygen-depleted and micro pore-decreased after the heating treatment. The mechanism of mercury adsorption in pure nitrogen follows the Mars–Maessen mechanism over the carbon sorbents. To identify the effects of carbon monoxide (CO) and carbon dioxide (CO\textsubscript{2}) on Hg\textsuperscript{0} removal, the Hg\textsuperscript{0}-adsorption and thermal desorption experiments were carried in a fixed-bed reaction system. CO inhibits both the chemisorption and physisorption of Hg\textsuperscript{0}. CO\textsubscript{2} competes for the active sites, lactone groups and hydroxyl groups, and occupies the micropores, which is beneficial for adsorb Hg\textsuperscript{0} physically. When CO and CO\textsubscript{2} coexisted, the removal efficiencies show steadier than those in monocomponent gas (only CO or CO\textsubscript{2}). CO\textsubscript{2} can resist the negative effect of CO on Hg\textsuperscript{0} removal, to some extent, because CO\textsubscript{2} can inhibit the oxidation and disproportionation of CO. This experimental study provides practical guidance for the development of mercury-removal technology with carbon materials in the coal gasification plant.

INTRODUCTION

World Health Organization (WHO) has picked out mercury as one of chemicals of the major public health concern for its high toxicity.\textsuperscript{1} Mercury is the only heavy metal participating in the atmospheric cycle, which can transport for a long distance in the form of gaseous Hg\textsuperscript{0}. In ecosystems, such as soils, sediments, and aquatic systems, elemental mercury can partly convert into methylmercury (MeHg), which can readily bioaccumulate in the bodies of aquatic animals.\textsuperscript{2,3} When people consume a contaminated fish and seafood, MeHg can get into the human body and damage the central nervous system or even cause death in a condition of severe exposure.\textsuperscript{4,5} Anthropogenic sources emitted 2220 tons of mercury to the atmosphere in 2015,\textsuperscript{6} and coal-burning was responsible for nearly 21%.\textsuperscript{6} Global coal consumption made up 27% in primary energy in 2019, which is the lowest level in 16 years, but coal remains as the dominant energy source in some emerging countries with huge economic development demands, particularly in China, Indonesia, and Vietnam.\textsuperscript{7} Thus, more attention should be given to reduce mercury emissions during the process of coal utilization.

In recent years, gasification has become a core technology for the high-efficient and clean utilization of coal resources. Coal, or mixed with biomass,\textsuperscript{8,9} reacts with gasification agents at about 700 °C, and then it is converted into synthesis gas (syngas) consisting of carbon monoxide, carbon dioxide, and hydrogen. These gaseous products are used for combusting for advanced power generation,\textsuperscript{10,11} producing fine chemicals,\textsuperscript{12} or synthesizing fuel via the Fischer–Tropsch process.\textsuperscript{13} The predominant species of mercury, releasing from coal, among the gaseous products is Hg\textsuperscript{0} due to the high temperatures and reducing atmospheres.\textsuperscript{14–16} Given that Hg\textsuperscript{0} has high volatility and low solubility in water, capturing elemental mercury with heterogeneous catalytic adsorbents,\textsuperscript{17–19} especially modified carbon materials, is one of the favorable methods. CO\textsubscript{2} needs to be separated from syngas and condensed for storage to reduce the greenhouse effect, but trace mercury in CO\textsubscript{2} stream can corrode aluminum equipment\textsuperscript{20,21} when it flows through purification and compression units. Also, mercury poisons metal catalysts in synthetic reactions.\textsuperscript{22} It is necessary to remove mercury after the pyrolysis process considering the endangerment of mercury.

Porous carbon materials are widely used in the removal of pollutants from the exhaust gases because they have flourishing pore structures and prodigious surface areas as well as plentiful functional groups. Hydrocarbon functional groups can activate neighboring carbon atoms and promote the capacity of carbonaceous surfaces for Hg\textsuperscript{0} removal.\textsuperscript{23} Meanwhile, it has been reported that the C=O groups in carbonyl groups (C==O) and ester groups (C(O)–O–C) could oxidize Hg\textsuperscript{0} and...
turn into C=O, while phenol and carboxyl groups could adsorb mercury physically.

The performance of two gases over a carbonaceous adsorbent surface has been evaluated by experiments and DFT simulations. The micropore diffusivity of CO in activated carbon is faster than CO$_2$'s at 303 K, but the order of the stabilities is just the opposite. In addition, when CO concentration is high, it competes with Hg$^0$ for adsorption sites, and CO$_2$ does not disturb the mercury adsorption.

Shen et al. supposed CO has a negligible effect on a CuCl$_2$-AC sorbent, whereas other researchers have suggested CO takes a passive role because it can generate deposited carbon over the adsorbent surface and block the pore structures. The CO$_2$ concentration in the syngas varies from 7 to 40 vol %.

In this work, activated cokes were pretreated under different timings at 1000 °C for further study. The removal of Hg$^0$ was investigated in a laboratory-scale fixed-bed reactor, and the adsorption products were identified by the temperature-programmed desorption (TPD). Moreover, the characterization methods of the fresh and used sorbents were as follows: scanning electron microscope (SEM), Brunauer–Emmett–Teller (BET), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR). The influence of CO and CO$_2$ on activated cokes was discussed.

### RESULTS AND DISCUSSION

#### Characterization of Activated Cokes

Figure 1 shows the microphotographs of activated cokes with different heating times under 1000 °C. The surface of the raw activated coke is rich in porosity, but the high temperature flattened the other surface.

The parameters of the pore structure of ACs are shown in Table 1, the branches of isotherms are shown in Figure 2a, and the pore distributions are presented in Figure 2b. AC had the largest specific surface area (470.5 m$^2$/g); the microporous areas of two calcined ACs dropped by more than 50%, compared with the raw AC. The curves in Figure 2a have hysteresis loops, the characteristic feature of mesoporous matters, which means they belong to Type IV isotherms. Figure 2b exposes that the pore diameters of three kinds of activated cokes were mainly disturbed in the range of 0–2.0 nm (micropores) and 2–20 nm (mesopores). An excessively pretreating temperature (1000 °C) caused the microporous walls to collapse, but the mesopores were developed during heating duration. The longer the heating process, the larger the mesoporous volume. It may explain the relative extension in the total volume of AC10 compared with AC2.

The kinetic diameter of mercury is 0.30 nm. The pores, whose diameters are in the range of 0.5–0.9 nm, are suitable for adsorbing mercury atoms in a physical way, according to the adsorption theory. The micropore volume of AC2 in that range (Figure 2b) is close to that of AC10, which implies that its mercury physisorption capacity is similar.

FTIR (Figure 3) was carried out to explore the functional groups over the carbonaceous surfaces in the study. The broad peak at 3600–3200 cm$^{-1}$ is from the stretching vibration of self-associated O–H or pyrrolic N–H; a sharp peak at 3642 cm$^{-1}$ in AC2 and AC10 is related to a free or unassociated hydrogen bond of –OH among molecules. The peaks at 2960, 2922, and 2854 cm$^{-1}$ belong to stretching vibration of C–H in –CH$_3$, –CH$_2$–, and –CH=, respectively. These peaks of AC, AC2, and AC10 (Figure 3) indicate that the intensity of aliphatic hydrocarbons was of positive correlation with the heating time. The population of aliphatic hydrocarbons enlarged when purged in the CO atmosphere. It demonstrates that CO could directly react with oxygen-containing functional groups increasing the content of saturated carbon at 80 °C. The physical adsorption of CO$_2$ forms the peaks at 2300–2400 cm$^{-1}$. The vibration peaks at 1775–1345 cm$^{-1}$ are identified as the oxygen-containing functional groups (carbonyl and lactone) vibration and aromatic C=C stretching vibration. The distribution of the peaks of purged AC2s among this zone differs from the fresh AC2, which emphasizes that CO and CO$_2$ would react with the oxygen-groups that are involved in the oxidation of mercury. The peaks at 877 and 798 cm$^{-1}$ represent the substituted benzene ring with isolated hydrogen and two neighboring hydrogen or angular condensation ring systems. The types and numbers of oxygen-containing functional groups greatly changed during the heating treatment. Therefore, the influence of CO and CO$_2$ should not be ignored when studying the mercury-removal capacity of activated cokes.

#### Table 1. Textural Properties of AC, AC2, and AC10

| sample | micropore (<2 nm) | mesopore (2–50 nm) | total pore | average pore diameter (nm) |
|--------|------------------|-------------------|------------|---------------------------|
|        | $V_{mic}$ (cm$^3$/g) | $S_{mic}$ (m$^2$/g) | $V_{mes}$ (cm$^3$/g) | $S_{mes}$ (m$^2$/g) | $V_{total}$ (cm$^3$/g) | $S_{total}$ (m$^2$/g) | |
| AC     | 0.14             | 334.0             | 0.20       | 136.0         | 0.37             | 470.5 ± 1.5         | 5.9         |
| AC2    | 0.05             | 110.2             | 0.18       | 127.1         | 0.27             | 263.5 ± 0.8         | 6.0         |
| AC10   | 0.07             | 160.4             | 0.22       | 152.1         | 0.32             | 332.9 ± 0.6         | 5.9         |

Figure 1. SEM images for (a, b) AC, (c, d) AC2, and (e, f) AC10.
XPS analysis was taken to characterize the surface functional groups and their proportions on the surface of the samples with different treatments. The multipeaks of C1s and O1s were simulated by Avantage software, and the atomic concentrations of two elements were calculated at the same time. The relevant data are shown in Figure 4 and Table 2.

Figure 2. Nitrogen-adsorption–desorption isotherms (a) and distribution of pore size (b) of AC, AC2, and AC10.

The C1s peak could be recognized as five main types:37–39 (C-graphite (∼284.8 eV), the C in C−O bonding (∼285.5 eV), the carbonyl carbon (∼288.0 eV), the carboxylate C (C(O)O, ∼289.1 eV), and π−π* (∼291.2 eV). The relative intensity of the carbonyl carbon drops from 5.2% (AC) to 0.8% (AC2), and the relative intensity of the carboxylate carbon lifts from 2.5% (AC) to 7.7% (AC2). As carbonyl and lactone groups can oxidize mercury in the temperature range of 30−210 °C,40 the loss of C≡O would negatively impact the capturing process of Hg0 but the increment of C(O)O would do the opposite. It coincides with the adsorption experiment results that the Hg0-removal efficiencies of AC and AC2 were close (53.46 and 49.31%, respectively). AC2 lost the major physical adsorption capacity, but the increase of C(O)O covered the loss. Also, the C≡O and C(O)O proportions of AC2-CO were 0.2 and 6.4%, these fractions in AC2-CO2 were 1.1 and 6.8%, and their percentages of AC2-CO/CO2 were 0.9 and 4.9%. These discrepancies show that CO could decay the C≡O but CO2 enhance it, and both gases would reduce the contents of C(O)O. When AC2 processed with CO and CO2 together, the effects of both sides on C≡O could be counteracted, but the adverse impact on C(O)O would be worsened.

The O elemental mainly exists in four forms as follows:38 C≡O (∼532.1 eV), C−O (∼533.1 eV), −OH (∼534.2 eV),

Figure 3. FT-IR spectra of different activated coke samples (AC2-CO: AC2 purged by CO for 3 h at 80 °C, AC2-CO2: AC2 purged by CO2 for 3 h at 80 °C, AC2-CO/CO2: AC2 purged by CO and CO2 for 3 h at 80 °C, used AC2: AC2 used in the adsorption experiment in N2 for 2 h at 80 °C).

Figure 4. C1s and O1s XPS spectra of (a)−(c) AC2, (c, d) AC2-CO, (e, f) AC2-CO2, (g, h) AC2-CO/CO2, and (i, j) used AC2.

Figure 2. Nitrogen-adsorption–desorption isotherms (a) and distribution of pore size (b) of AC, AC2, and AC10.
Mercury-Removal Performance. The mercury-removal efficiencies of different types of active cokes under the nitrogen atmosphere are illustrated in Figure 5. The Hg\(^0\)-removal efficiencies at 80 °C of AC, AC2, and AC10 are 53.46, 49.31, and 10.03%, respectively. The higher temperature restrained the performance of AC2 in nitrogen.

![Figure 5. Mercury average-removal efficiencies of AC and ACs within 2 h in nitrogen.](https://dx.doi.org/10.1021/acsomega.0c05260)

The terrible performance of AC10 could be interpreted by the poor physical adsorption and low oxygen contents. As mentioned above (Table 1), the low microporous volume of AC10 determined its terrible physical adsorption.\(^{41,42}\) The drop of oxygen species is due to the prolonged heating duration. The oxygen–carbon (O/C) ratio is 0.06 over the surface of AC10, which is approaching to the used AC2’s. The active oxygen comes from free oxygen and oxygen-containing functional groups (carbonyls, lactones, etc.).\(^{40}\) and the amount of active oxygen is relative to the intensity of chemisorption. Thus, AC and AC2 show a better performance than AC10.

In a pure nitrogen atmosphere, the chemical adsorption of Hg\(^0\) would follow the Mars–Maessen mechanism.\(^{45,44}\) The specific reaction formula is as follows:

\[
\text{Hg}(g) + \text{surface} \rightarrow \text{Hg(ads)} \quad \text{(R1)}
\]

\[
\text{Hg(ads)} + \text{O(ads)} \rightarrow \text{HgO} \quad \text{(R2)}
\]

As AC2 and AC10 are in a similar distribution of the micropores, which play an important role in physisorption, it could be deduced that chemical adsorption of AC2 is the dominant one. Within the temperature range of 80–120 °C, the efficiency decreases notably as the temperature increases. The results are consistent with the reported literature data.\(^{40}\) It is thought that the higher temperature could supply sufficient energy for the Hg\(^0\) oxidation, but the results are the exact opposite. The higher temperature does no favor to the physisorption, which is exothermic, so mercury atoms have less possibility to stay on the surface. The first reaction R1 was restrained at the higher temperature, and, of course, the second reaction R2 could hardly take place when Hg\(^0\) could hardly get close to the active oxygen.

Since AC2 has enough oxygen-containing functional groups and not enough micropore structure, it is a suitable adsorbent for exploring the effects of CO and CO\(_2\) on the carbonaceous surface. All the adsorbents used in the subsequent experiments are AC2 without special notification.

### Mercury-Removal Activities in CO Atmosphere

CO is one of the main components of coal gasification products. Studying the effect of CO on the mercury-removal performance can provide the suggestions for the application of adsorbents in a reducing atmosphere. The average Hg\(^0\)-adsorption efficiency of AC2 is dotted in Figure 6, in various concentrations of CO within 1 h at 80 °C.

![Figure 6. Hg\(^0\)-removal efficiency of various CO concentrations within 1 h at 80 °C.](https://dx.doi.org/10.1021/acsomega.0c05260)
respectively. No question that CO inhibited Hg⁰ removal, and the main reasons are as follows:

1. The CO purging treatment may decline the quantity of oxygen-containing functional groups and free oxygen on the surface of AC based on Table 2. CO could compete with Hg⁰ for the active oxygen (carbonyls and lactones, especially), impeding the mercury (R4R4).

\[
\text{CO(g)} + \text{O(ads)} \rightarrow \text{CO}_2 \\
\text{Hg}^0 + \text{O(ads)} \rightarrow \text{HgO}
\]

The following experiment was carried out to prove the deduction. An amount of 0.1 g of AC2 was placed in a quartz tube on the fixed-bed reactor. Then, the AC2 adsorbent was purged with CO at a flow rate of 400 mL/min for an hour at 80 °C. The treated AC2, named as AC2-CO1, was used in adsorption experiments in nitrogen at 80 °C.

The adsorption curves of AC2-CO1 and fresh AC10 are pictured in Figure 7. The adsorption curves converge together with time. The average adsorption efficiency of AC2-CO1 is only 8.28%. It meets the conclusion that the oxidation of Hg⁰ may slow down due to CO.

2. The inverse reaction of Boudouard reaction (R5R5) could take place. CO may transform into CO₂ and graphite, and the latter would deposit on the pore structures.

\[
\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO(g)}
\]

When the reaction temperature rose to 120 °C, black deposits were observed on the inner wall of the quartz tube. When the quartz tube with a black substance was heated in air at a high temperature (1000 °C) for a moment, the black substance did not appear during the adsorption experiment in an N₂ atmosphere at 120 °C. The black substance should be graphite.

3. CO, the strong reducing agent, would facilitate the formation of low valence states mercury (R6R6). This part is discussed further in Thermal Desorption Experiments.

\[
\text{CO(g)} + \text{HgO} \rightarrow \text{CO}_2(g) + \text{Hg}
\]

Mercury-Removal Activities in a CO₂ Atmosphere.
Trace mercury can corrode the aluminum equipment in the carbon capture process. It is essential to remove mercury from the gas before gathering CO₂. Figure 8 shows that Hg⁰ removal efficiencies in CO₂ stay at about 30%. CO₂ also has a negative impact on the adsorption of element mercury.

The Hg⁰ average-removal efficiencies of 20% CO/5% CO₂, 20% CO/10% CO₂, and 20% CO/20% CO₂ are 14.97, 22.68, and 29.83% within 1 h at 80 °C. With the proportion of CO₂ increases, the adsorption efficiency enhances accordingly. When the experiment atmosphere contained only CO or
only CO₂, their adsorption efficiencies are higher than those of the CO and CO₂ coexisting experiments at first. Soon the efficiencies of single-gas experiments (CO or CO₂) fall rapidly from 74.62% (CO) and 56.30% (CO₂) to below 30% at 20 min, whereas the efficiencies of dual-gas experiments (CO coexisting with CO₂) remain parallel with the x-axis.

As mentioned above, CO₂ would cut off the path to physisorption and chemisorption of mercury. The higher concentration of CO₂ in the dicomponent experiments, the more Hg₀-adsorption sites occupied at the first 5 min. It made the 20% CO/20% CO₂ group to have the lowest efficiency at first.

As one of the products in the inverse Boudouard reaction (R5R5) and the reduction reaction of HgO, CO₂ could limit the disproportionation reaction of CO and the higher CO₂ concentration could protect the divalent mercury from reducing. CO₂ only occupied the active sites physically; as the reactions proceeding, the active oxygen would be released and react with Hg₀.

Considering the high amounts of CO and CO₂ in gasification products, it is reasonable to purify the gas before separating the syngas because CO₂ could promote the adsorbent performance when CO exists.

**Thermal Desorption Experiments.** Different mercury-containing compounds can be converted to elemental mercury at different temperatures and flow out with the gas, so the species and portions of mercury were analyzed by thermal desorption experiments.

After adsorbing and purging process, the adsorbents were heated in N₂ at a flow rate of 0.25 L/min, and the temperature was programmed at the rate of 3 °C/min from 80 to 500 °C. The different purging conditions and distribution of various mercury components are given in Table 3. The temperature-programmed desorption curves are displayed in Figure 10. AC₂ purged with N₂ has two obvious desorption peaks, which are at 195 and 280 °C.

The mercury-adsorption capacity of AC10 can be approximatively considered as physical adsorption. The physical adsorption amount of AC₂ can be thought as same as AC₁₀’s due to their similar microporous structures. The total adsorption amount of 0.1 g AC10 for 2 h in N₂ is 0.82–1.56 μg. Supposing that the physical and chemical adsorption contents did not change after purging in nitrogen, the mercury content of the peak at 195 °C in group d is 1.24 μg, which is in the range of the total adsorption amount of AC₁₀. Therefore, the desorption peak at 195 °C is attributed to physical adsorption. In Hong’s study, the desorption peak of physical adsorption was at 160 °C. The difference is related to the purging time of the desorption experiment and the flow rate of the desorption carrier gas.

The decomposition temperature range of HgO is between 200 and 380 °C, and the decomposition temperature range of HgS is between 180 and 350 °C. But neither the active cokes nor the experimental atmosphere contained the sulfur, so the desorption peak at 280 °C is attributed to HgO.

After adsorbing in nitrogen, the used activated cokes were separately purged with a mercury-free CO gas for 1 h (Figure 10c) and 5 h (Figure 10b). The proportion of desorption products corresponding to the 280 °C peak decreases from 61.33 to 52.8% (CO, 1 h) and 19.1% (CO, 5 h). Furthermore,
the ratio of the purged amount to the total adsorption of group d is only 18.9%, which is much lower than the ratio of groups b and c (39.6%, 44.3%). These results prove that CO could directly reduce high-valence mercury as R8R8.

The adsorption curve of AC2-CO1 (Figure 7) points out that CO purging treatment can cause the depletion of the adsorption performance of fresh AC. The adsorption amount of group a (0.34 μg) is only one-tenth of that of group d (3.22 μg). Not only AC2-CO1 had a poor chemical adsorption capacity but also its physical adsorption performance was weakened, which supports the view that CO disproportionation reaction can happen.

**CONCLUSIONS**

With the adsorption and temperature-programmed desorption, the mechanisms of CO and CO2 on the Hg0-removal performance of calcined activated cokes have been analyzed and verified. The conclusions are as follows:

1. The prolonged heating time can destroy micropores and the C═O but generate C(O)O and the saturated carbon. The chemical adsorption of Hg0, with oxygen functional groups, follows the Mars—Maessen mechanism in N2, and the reactions are vulnerable to temperature changes. The mercury-removal efficiencies of AC2 dived when the temperature rose to 120 °C.
2. CO could react with functional groups, especially C═O. It could reduce HgO directly and decompose into graphite blocking the microporous structures.
3. CO2 impedes the Hg0 oxidation through occupying the active sites and micropores physically.
4. When adding CO and CO2 into the same system, CO2 would slow down the negative effect of CO on mercury removal. The tendency of the removal efficiencies in dicomponent groups was stabilized after the first 10 min.
5. The desorption peak at 195 °C is attributed to physical adsorption, and the one at 280 °C belongs to chemical adsorption.

Due to the performance of AC2 in the dicomponent experiments, it would be better to remove mercury from the gasification products before syngas processing and usage. Further investigations are needed in developing a detailed mechanism of multiple reactants at the atomic level.

**MATERIALS AND METHODS**

**Preparation of Activated Cokes.** The activated coke was purchased from the Henan Ultra-clean Water Treatment Technology Co., Ltd. (China). The activated coke was crushed and sifted through 60−80 mesh, washed with distilled water, and then dried in an oven at 110 °C for 24 h. The dried coke was named as AC. Afterward, two groups of AC were calcined to remove oxygen-containing functional groups under the N2 atmosphere for 2 and 10 h, respectively; and the resulting products were designated as AC2 and AC10.

**Mercury Adsorption and TPD Experiments.** All the adsorption experiments were performed on a fixed-bed catalytic reactor, as shown in Figure 11. A mercury vapor generating device (Valco Instruments Company Inc., the U.S.) was used to provide a constant initial concentration (50 μg/m3) of elemental mercury vapor carried by high-purity N2. The mixture contained CO (20, 30, or 40 vol %) and CO2 (5, 10, or 20 vol %), and the balance gas was N2. All the gases were precisely controlled by mass flowmeters (Beijing Sevenstar Electronics Co., Ltd., China). The total gas flow rate was 1.2 L/min in adsorption experiments; in other words, the gas hourly space velocity (GHSV) was approximately 120,000 h−1. The concentrations of mercury were accurately measured by a continuous mercury emissions monitor, Tekran 3310Xi (Tekran Instruments Corporation, the U.S.), whose sampling interval is 150 s. A 0.1 g sample was used in each test when the adsorption or purging process in the same reactor. The steps were as follows. First, the used adsorbent was purged with nitrogen gas (1 L/min) until the mercury concentration was low enough, and the time of this step lasts as required.

The TPD experiments were started instantly after the adsorption or purging process in the same reactor. The steps were as follows. First, the used adsorbent was purged with nitrogen gas (1 L/min) until the mercury concentration was low enough, and the time of this step lasts as required.
less than 2 \( \mu g/m^3 \) at the outlet. Second, while nitrogen (250 mL/min) flew through the gas lines, the desorption temperature increased from 80 to 500 °C at the rate of 3 °C/min. In the desorption experiment, the outlet mercury concentration was monitored in real-time by RA 915+ (Lumex Instrument, Russia), whose sampling interval was 1 s.

Tekran 3310Xi can monitor Hg\(^0\) and Hg\(^{2+}\) at the same time. During the adsorption experiments, the amount of Hg\(^{2+}\) was too low to consider. The mercury-removal efficiency (\( \eta \)) of the adsorbent is defined as:

\[
\eta = \left( e_{in} - e_{out} \right) / e_{in} \times 100\%
\]

In the equation, \( e_{in} \) and \( e_{out} \) are the Hg\(^0\) concentration at the inlet and outlet of the reactor (\( \mu g/m^3 \)), respectively.

The mercury average-removal efficiency is defined as the average value of \( \eta \) in a certain period.

In the thermal desorption experiment, the definitions of the mercury-adsorption amount (\( m_{ads} \)), purging amount (\( m_{purge} \)), and desorption amount (\( m_{des} \)) are as follows:

\[
m = \left( e_{in} - e_{out} \right) \times v \times \Delta t
\]

In this formula, \( \Delta t \) is the desorption time (s); \( v \) is the total gas flow rate (m\(^3\)/s). The influence of thermodynamic factors on gas volume was neglected in this work.

Vent gas went through the off-gas treatment system before discharged into the air.

**Characterization of Activated Cokes.** The morphology of ACs was photographed by a field emission scanning electron micrograph (German Carl Zeiss, Sigma 500).

Nitrogen-adsorption isotherms were measured at -196.3 °C on physisorption analyzers (US Micromeritics Instruments Corporation, ASAP 2020) and so were the specific surface area and pore parameters of the sorbents. The pretreatment was degassing samples at 250 °C for 3 h. The total pore surface area (\( S_{total} \)) was derived from the Brunauer–Emmett–Teller method fitting for values of relative pressure (\( p/p^0 \)) ranging from 0.05 to 0.35, while the total pore volume (\( V_{total} \)) used single-point total pore volume evaluation at \( p/p^0 = 0.99 \). The average pore diameter and volume (\( V_{mic} \)) and area (\( S_{mic} \)) of mesopore were calculated by the Barrett–Joyner–Halenda (BJH) algorithm with the data of the desorption branch of the isotherm. The volume (\( V_{mic} \)) and area (\( S_{mic} \)) of the micropore were deducted from the t-plot analysis. Meanwhile, the DFT model was applied for the porosity distribution.

The elemental valence states were obtained by an X-ray photoelectron spectrometer (Thermo Fisher Scientific, ESCALAB 250Xi) with an Al K-Alpha X-ray source. The CIs binding energy value (284.8 eV) helped to calibrate the results.

To investigate the functional groups, samples were blended with potassium bromide (KBr) powders, then pressurized into thin slices to 15 MPa for 10 min by a tablet machine, and detected by Fourier transform infrared spectroscopy (Thermo Fisher Scientific, Nicolet iS10) at last. The resolution was set to be 4.0 cm\(^{-1}\), and the detection range was from 500 to 4000 cm\(^{-1}\).

### Authors

**Qixin Zhou** — State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University, Hangzhou 310027, P. R. China

**Hui Cao** — State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University, Hangzhou 310027, P. R. China

**Xinyu Xu** — State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University, Hangzhou 310027, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c05260

**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

We express our thanks to the National Nature Science Foundation of China (no.51576173) for their support.

### REFERENCES

(1) WHO International Programme on Chemical Safety; WHO: Geneva, [https://www.who.int/health-topics/chemical-safety#tab=tab_1](https://www.who.int/health-topics/chemical-safety#tab=tab_1)

(2) Järup, L. Hazards of mercury—safety perspectives and measures. Br. Med. Bull. 2003, 68, 167–182.

(3) Backstrom, C. H.; Buckman, K.; Molden, E.; Chen, C. Y. Mercury Levels in Freshwater Fish: Estimating Concentration with Fish Length to Determine Exposures Through Fish Consumption. Arch. Environ. Contam. Toxicol. 2020, 78, 604–621.

(4) Bravo, A. G.; Cosio, C. Biotic formation of methylmercury: A bio–physico–chemical conundrum. Limnol. Oceanogr. 2020, 65, 1010–1027.

(5) Clarkson, T. W. Mercury: major issues in environmental health. Environ. Health Perspect. 1993, 100, 31–38.

(6) AMAP/UN Environment Technical Background Report for the Global Mercury Assessment 2018. In Arctic Monitoring and Assessment Programme; Oslo, Norway/UN Environment Programme, Chemicals and Health Branch: Geneva, Switzerland, 2019; pp. 1–430.

(7) Looney, B. BP statistical review of world energy; 69th ed; BP Statistical Review: London, UK, 2020; pp 3–1.

(8) Minchener, A. J. Coal gasification for advanced power generation. Fuel 2005, 84, 2222–2235.

(9) Guo, F.; He, Y.; Hassanpour, A.; Gardy, J.; Zhong, Z. Thermogravimetric analysis on the co-combustion of biomass pellets with lignite and bituminous coal. Energy 2020, 197, 117147.

(10) Wang, D.; Li, S.; Gao, L.; Wu, H.; Jin, H. Novel coal-steam gasification with a thermochemical regenerative process for power generation. J. Energy Resour. Technol. 2018, 140, No. 092203.

(11) An, D.; Wang, X.; Cheng, X.; Cui, L.; Zhang, X.; Zhou, P.; Dong, Y. Regeneration performance of activated coke for elemental mercury removal by microwave and thermal methods. Fuel Process. Technol. 2020, 199, 106303.

(12) Lamaison, S.; Wakerley, D.; Montero, D.; Rousse, G.; Taverna, D.; Giaume, D.; Mercier, D.; Blanchard, J.; Tran, H. N.; Fontecave, M. Zn–Cu Nanofoams as Efficient Catalysts for the Reduction of CO\(_2\) to Syngas Mixtures with a Potential-Independent H\(_2\)/CO Ratio. ChemSusChem 2019, 12, 511–517.

(13) Atashi, H.; Veiskarami, S. Green fuel from coal via Fischer–Tropsch process: scenario of optimal condition of process and modelling. Int. J. Coal Sci. Technol. 2018, 5, 230–243.

(14) Zhao, S.; Pudasainee, D.; Duan, Y.; Gupta, R.; Liu, M.; Lu, J. A review on mercury in coal combustion process: Content and occurrence forms in coal, transformation, sampling methods, emission and control technologies. Prog. Energy Combust. Sci. 2019, 73, 26–64.
(15) Lu, D. Y.; Granatstein, D. L.; Rose, D. J. Study of mercury speciation from simulated coal gasification. Ind. Eng. Chem. Res. 2004, 43, 5400–5404.

(16) Li, Y.; Zhang, J.; Zhao, Y.; Zheng, C. Volatilization and speciation of mercury during pyrolysis and gasification of five Chinese coals. Energy Fuels 2011, 25, 3988–3996.

(17) Chen, Y.; Guo, X.; Wu, F. Development and evaluation of magnetic iron-carbon sorbents for mercury removal in coal combustion flue gas. J. Energy Inst. 2020, 93, 1615–1623.

(18) Shen, F.; Liu, J.; Dong, Y.; Wu, D.; Gu, C.; Zhang, Z. Elemental mercury removal from syngas by porous carbon-supported CuCl2 sorbents. Fuel 2019, 239, 138–144.

(19) Quiros-Alvarez, M.; Diaz Somoano, M.; Bongartz, W.; Vinjarapu, S. Mercury interaction on modified activated carbons under oxyfuel combustion conditions. Energy Fuels 2018, 32, 5405–5408.

(20) Wang, J.; Wang, J.; Zhang, Y.; Wang, T.; Pan, W. P. Ionic mercury captured by H2S sulfured biochar in liquid hydrocarbons: Mechanism and stability evaluation. Fuel 2020, 278, 118413.

(21) Mitsui, Y.; Imada, N.; Kikkawa, H.; Katagawa, A. Study of Hg and SO2 behavior in flue gas of oxy-fuel combustion system. Int. J. Greenhouse Gas Control 2011, 5, S143–S150.

(22) Qin, H.; He, P.; Wu, J.; Chen, N. Theoretical study of hydrocarbon functional groups on elemental mercury adsorption on carbonaceous surface. Chem. Eng. J. 2020, 380, 122505.

(23) Zhang, B.; Xu, P.; Qiu, Y.; Yu, Q.; Ma, J.; Wu, H.; Luo, G.; Xu, M.; Yao, H. Increasing oxygen functional groups of activated carbon with non-thermal plasma to enhance mercury removal efficiency for flue gases. Chem. Eng. J. 2015, 263, 1–8.

(24) Hong, D.; Zhou, J.; Hu, C.; Zhou, Q.; Mao, J.; Qin, Q. Mercury removal mechanism of AC prepared by one-step activation with ZnCl2. Fuel 2019, 235, 325–335.

(25) Liu, J.; Cheney, M. A.; Wu, F.; Li, M. Effects of chemical functional groups on elemental mercury adsorption on carbonaceous surfaces. J. Hazard. Mater. 2011, 186, 108–113.

(26) Lopes, F. V. S.; Grande, C. A.; Ribeiro, A. M.; Loureiro, J. M.; Pinheiro, P.; Geraldes, O.; Rodrigues, J.; Rodrigues, J. M. Evaggelos, O.; Nikolaikis, V.; Rodrigues, A. E. Adsorption of H2, CO, CH4, CO2, N2, and H2O in activated carbon and zeolite for hydrogen separation. Sep. Sci. Technol. 2009, 44, 1045–1073.

(27) Wenqi, Q. Study on Heavy Metals Online Monitoring, Release and Adsorption Mechanism during Combustion; Hunghang University of Science and Technology: Wuhan, China, 2013; pp. 100–164.

(28) Pinheiro, P.; Schuler, M. C.; Gidelle, P.; Mermoux, M.; Dooryhee, E. Effect of hydrogen on the orientation of carbon layers in deposits from the carbon monoxide disproportionation reaction over Co/Al2O3 catalysts. Carbon 2000, 38, 1469–1479.

(29) Corbetta, M.; Bassani, A.; Manenti, F.; Pirolo, C.; Maggio, E.; Pettinau, A.; Deiana, P.; Pierucci, S.; Ranzi, E. Multi-scale kinetic modeling and experimental investigation of syngas production from coal gasification in updraft gasifiers. Energy Fuels 2015, 29, 3972–3984.

(30) Fisher, J. C., II; Sirlirawadee, R. V.; Stevens, R. W., Jr. Process for CO2 capture from high-pressure and moderate-temperature gas streams. Ind. Eng. Chem. Res. 2012, 51, 5273–5281.

(31) Hong, Y. C.; Lee, S. J.; Shin, D. H.; Kim, Y. J.; Lee, B. J.; Cho, S. Y.; Chang, H. S. Syngas production from gasification of brown coal in a microwave torch plasma. Energy 2012, 47, 36–40.

(32) Diamantopoulou, I.; Skodras, G.; Sakellaropoulos, G. P. Sorption of mercury by activated carbon in the presence of flue gas components. Fuel Process. Technol. 2010, 91, 158–163.

(33) Klobes, P.; Meyer, K.; Munro, R. Poreosity and Specific Surface Area Measurements for Solid Materials; Special Publication 960–17. US Department of Commerce, National Institute of Standards and Technology: Washington, DC, 2006.

(34) Svehla, R. A. Estimated viscosities and thermal conductivities of gases at high temperatures; National Aeronautics and Space Administration: 1963; Vol. 132, p 22.

(35) Li, X.; QIN, Z. H.; BU, L. H.; Yang, Z.; SHEN, C. Y. Structural analysis of functional group and mechanism investigation of coking property of coking coal. J. Fuel Chem. Technol. 2016, 44, 385–393.

(36) Shen, W.; Li, Z.; Liu, Y. Surface chemical functional groups modification of porous carbon. Recent Pat. Chem. Eng. 2008, 1, 27–40.

(37) Shao, G.; Lu, Y.; Wu, F.; Yang, C.; Zeng, F.; Wu, Q. Graphene oxide: the mechanisms of oxidation and exfoliation. J. Mater. Sci. 2012, 47, 4400–4409.

(38) Okpalugo, T. I. T.; Papakonstantinou, P.; Murphy, H.; McLaughlin, J.; Brown, N. M. D. High resolution XPS characterization of chemical functionalised MWCNTs and SWCNTs. Carbon 2005, 43, 153–161.

(39) An, D.; Sun, X.; Cheng, X.; Cui, L.; Zhang, X.; Zhao, Y.; Dong, Y. Investigation on mercury removal and recovery based on enhanced adsorption by activated coke. J. Hazard. Mater. 2020, 384, 121354.

(40) Sun, P.; Zhang, B.; Zeng, X.; Luo, G.; Li, X.; Yao, H.; Zheng, C. Deep study on effects of activated carbon’s oxygen functional groups for elemental mercury adsorption using temperature programmed desorption method. Fuel 2017, 200, 100–106.

(41) Skodras, G.; Diamantopoulou, I.; Zabaniotou, A.; Stavropoulos, G.; Sakellaropoulos, G. P. Enhanced mercury adsorption in activated carbons from biomass materials and waste tires. Fuel Process. Technol. 2007, 88, 749–758.

(42) Shen, F.; Liu, J.; Zhang, Z.; Dong, Y.; Yang, Y.; Wu, D. Oxygen-rich porous carbon derived from biomass for mercury removal: An experimental and theoretical study. Langmuir 2018, 34, 12049–12057.

(43) Mars, P.; Maessen, J. The mechanism and the kinetics of sulfur dioxide oxidation on catalysts containing vanadium and alkali oxides. J. Catal. 1968, 10, 1–12.

(44) Zhao, L.; Li, C.; Zhang, X.; Zeng, G.; Zhang, J.; Xie, Y. A review on oxidation of elemental mercury from coal-fired flue gas with selective catalytic reduction catalysts. Catal. Sci. Technol. 2015, 5, 3459–3472.

(45) Hunt, J.; Ferrari, A.; Lita, A.; Crosswhite, M.; Ashley, B.; Stiegemann, A. E. Microwave-specific enhancement of the carbon–carbon dioxide (Boudouard) reaction. J. Phys. Chem. C 2013, 117, 26871–26880.

(46) Liu, Y.; Wilcox, J. Effects of surface heterogeneity on the adsorption of CO2 in microporous carbons. Environ. Sci. Technol. 2012, 46, 1940–1947.

(47) Huang, X.; Chu, W.; Sun, W.; Jiang, C.; Feng, Y.; Xue, Y. Investigation of oxygen-containing group promotion effect on CO2–coal interaction by density functional theory. Appl. Surf. Sci. 2014, 299, 162–169.

(48) Li, J. R.; Kuppler, R. J.; Zhou, H. C. Selective gas adsorption and separation in metal–organic frameworks. Chem. Soc. Rev. 2009, 38, 1477–1504.

(49) Hu, X.; Radosz, M.; Cychoz, K. A.; Thommes, M. CO2-filling capacity and selectivity of carbon nanopores: synthesis, texture, and pore-size distribution from quenched-solid density functional theory (QSDFT). Environ. Sci. Technol. 2011, 45, 7068–7074.

(50) Presser, V.; McDonough, J.; Yeon, S.-H.; Gogotsi, Y. Effect of pore size on carbon dioxide sorption by carbide derived carbon. Energy Environ. Sci. 2011, 4, 3059–3066.

(51) Wu, S.; Uddin, M. A.; Nagano, S.; Ozaki, M.; Sasaoka, E. Fundamental study on decomposition characteristics of mercury compounds over solid powder by temperature-programmed decomposition sorption mass spectrometry. Energy Fuel 2011, 25, 144–153.