One-Step Preparation of Activated Carbon for Coal Bed Methane Separation/Storage and Its Methane Adsorption Characteristics

Yuannan Zheng, Shanshan Li,* Bingyou Jiang, Guofeng Yu, Bo Ren, and Haotian Zheng

ABSTRACT: Different coals were used as raw material for the preparation of carbonization precursors and coal-based activated carbons. The physicochemical structure and adsorption performance of the samples were tested. Results show that the carbonization and activation process greatly changed the molecular structure of raw coal, and a large number of organic functional groups disappeared. The carbonization process has enriched the pore structure of coal by thermal ablation, and it has a pore expansion effect on all the pores in coal, while the activation process is more conducive to micropore generation. The calculated mean isosteric heat of adsorption showed that the activated carbon needs to release more heat in the adsorption process as the same equilibrium pressure increased due to the adsorption capacity of the prepared activated carbon being far more than that of the raw coal. Adsorption processes of activated carbons are more sensitive to temperature changes, providing a certain guiding significance for the temperature swing adsorption and pressure swing adsorption.

1. INTRODUCTION

The original coal seam is rich in pores and fractures, where the methane (CH₄) widely exists. CH₄ is a great safety threat in coal mine production because of its inflammable and explosive property. Generally, CH₄ in coal seams is treated by drilling and extraction before coal seam mining. Since CH₄ is a clean energy source, the gas extracted from the coal seams can be used in principle. However, the coal seam occurrence conditions in China are relatively complicated, resulting in the CH₄ concentration in the gas extracted from coal seams being generally lower than 30%. Meanwhile, CH₄ is a strong greenhouse gas, and the gas released directly into the air can also cause environmental pollution. At present, there are many ways to produce low-concentration gas, which, after being purified by the pressure swing adsorption (PSA) or temperature swing adsorption (TSA) method, can be used as clean energy or chemical raw materials. An adsorbent with high capacities, high selectivity, and good regeneration ability is the key factor affecting the purification technology in the adsorption/desorption processes.

For a long time, carbon-based materials and zeolites have been widely studied for the separation and purification of various gases, while some new materials with a high specific surface area, such as metal–organic frameworks (MOFs), have gradually developed into research hotspots in recent years. However, new materials are limited by the high cost and complex production process, and activated carbon is still the most commonly used adsorbent material in civil and industrial applications. Coal and biomass materials (such as wood materials, fruit shells, agricultural wastes, and so on) contain a large amount of carbon, which can be used to prepare activated carbon. The physical activation method with water vapor as the medium, the chemical activation method with chemical reagents as the activator, and the physical–chemical activation method with the synergistic effect of physical and chemical methods, are the commonly used preparation methods of activated carbon. Raganati et al. had surface-modified carbon black (CB) and synthesized the novel carbon–magnetite composite sorbent. Based on the new sorbent, the CO₂ adsorption/desorption process on the ordinary and sound-assisted fluidized bed was analyzed from the perspective of kinetics and thermodynamics. Al Bahri et al. adopted the carbon dioxide activation method to prepare the activated carbons from the grape seeds. However, the pore structure of activated carbons prepared by the physical activation method is poorly developed as a result of the poor controllability. There are many researchers who have completed a great number of research studies and
found that high-performance activated carbons can be prepared by using KOH as an activating agent. Hüttinger,\textsuperscript{34} explained the reasons for the excellent activation effect of KOH activation on the preparation of activated carbon from the perspective of surface wettability. The liquid metal potassium produced by the reaction at high temperature reduces the tension of KOH on the surface of carbon-containing raw materials so that KOH reacts with carbon-containing raw materials more fully. The coal and bituminous mixtures were used as raw materials by Yao et al.,\textsuperscript{35} and activated carbon with a specific surface area of 672 m\textsuperscript{2}/g was prepared by the KOH chemical activation method. Li et al.\textsuperscript{36} first immersed the melon seed shells into KOH solution and, after that, activated them by carbon dioxide, and the activated carbon with a specific surface area of 2582 m\textsuperscript{2}/g was prepared. Coal is widely used because of its high yield and low price. A series of experiments were conducted by Lillo–Rodenas et al.\textsuperscript{37–39} to prepare the activated carbons by using anthracite as a precursor adopting the KOH activation method and found that micropores are preferentially formed during the high-temperature activation process at above 700 °C, which were subsequently continuously ablated to form mesopores and macropores. Therefore, the KOH activation method is an effective way to prepare activated carbons.

The preparation of activated carbon by chemical activation is divided into two processes: carbonization and activation. There are few reports on the effects of carbonization and activation on the coal matrix from the aspects of adsorption capacity and specific surface area. In this work, the CH\textsubscript{4} adsorption experiments for activated carbons from 273.15 to 373.15 K were, respectively, conducted on five different types of coal, the carbonized precursor, and coal-based activated carbons. The pore structure characteristics, adsorption performance, and thermodynamic properties of raw coal, the carbonization precursor, and coal-based activated carbon were compared and analyzed.

2. EXPERIMENTAL SECTION

2.1. Materials. The five different types of coal from low-rank bituminous to anthracite were selected and pulverized (the anthracite from the Guhanshan coal mine and Yangzhuang coal mine and the bituminous from the Dafosi coal mine, Shenmu coal mine, and Xinbei coal mine, respectively, represented by GHS, YZ, DF, SM, and XB). The proximate and vitrinite reflectance analyses of coal samples are shown in Table 1. First, the coal samples were sieved to obtain particles with the size range of 0.25–0.38 mm, and then, the particles were dried at 40 °C for 24 h in a drying oven as the raw materials. The chemical activation method was adopted to prepare activated carbons with a high specific surface area. The analytical pure KOH (produced by Sinopharm Chemical Reagent Co., Ltd in Shanghai, China) was used as an activator. From Table 1, the fixed carbon contents of selected coal samples are more than 50%, indicating that the coal samples have enough carbon content to ensure the formation of the pore structure and the yield of activated carbon.

2.2. Preparation of Coal-Based Activated Carbons. The preparation of activated carbon usually goes through two stages of carbonization and activation. In order to obtain a precursor with an initial pore structure and mechanical strength, the carbonization process should be preferentially carried out at a lower temperature. Then, the precursor is subjected to an activation process at high temperature, allowing the materials to acquire new pores and a larger specific surface area. Figure 1 shows the flow diagram of preparation of coal-based activated carbons. The raw materials and KOH were weighed separately and then mixed with a mass ratio of 1:3. The mixtures were put into two alumina crucibles, and then, they were placed in a tube furnace for carbonization and activation under a N\textsubscript{2} atmosphere. The carbonization and activation temperatures were set at 500 and 800 °C, respectively. First, the temperature was increased to 500 °C at the heating rate of 5 °C/min and then held for 120 min. Then, one of the crucibles was taken out and allowed to naturally cool to the ambient temperature under the protection of a nitrogen atmosphere. Another crucible was continuously heated to 800 °C also at 5 °C/min and then held for 120 min. After natural cooling to the ambient temperature, the samples were first treated with HCl solution with the mass concentration of 5% till the solution became acidic and then stirred for 6 h under 60 °C. Then, the samples were washed with deionized water till the PH meter shows that the solution is neutral. Finally, the carbonized precursors and coal-based activated carbons were obtained after drying at 40 °C for 24 h. All samples of coal, the carbonized precursor, and coal-based activated carbons were, respectively, marked as XX-Coal, XX-T500, and XX-AC (XX represents GHS, YZ, DF, SM, and XB). The scanning electron microscopy (SEM) images of the coal, carbonized precursor, and coal-based activated carbon are shown in Figure 2.

2.3. Characterization of Coal-Based Activated Carbons. 2.3.1. Pore Structure. The adsorption/desorption isotherms obtained by low-temperature nitrogen (77 K) adsorption experiments could be used to calculate the pore structure parameters of the samples, such as the specific surface area, pore volume, average pore size, and so forth. The automatic physical adsorption instrument (isorb-iQ, US) produced by Quantochrome Corporation was used, and the relative pressure was set in the range of 0.001–0.995. Before the test, the samples need to be dried and degassed at 105 °C for 8 h. Based on the tested isotherms, the specific surface area (S\textsubscript{BET}), total pore volume, micropore specific surface area, and micropore volume could be calculated by the Brunauer–Emmett–Teller (BET), Barrett–Joyner–Halenda (BJH), and t-plot methods.\textsuperscript{40–42} The pore size distributions (PSDs) were obtained using the non-local density functional theory (NLDFT).\textsuperscript{43}

2.3.2. Fourier Transform Infrared Spectral Measurements. Fourier transform infrared (FTIR) spectra were obtained using an infrared spectrometer (Invenio, GER) produced by Bruker Corporation, and the resolution was set at 4 cm\textsuperscript{−1} in the

| Sample | FC\textsubscript{ad} (w/w %) | VM\textsubscript{ad} (w/w %) | \( \beta_{ad} \) | \( M_{ad} \) | \( R_{\text{max}} \) (vitrinite) | Yield of \( \beta \) (coal-based carbons) |
|--------|------------------|--------------------|-------------|-------------|-----------------|-------------------------------|
| GHS    | 83.35            | 7.68               | 6.48        | 2.49        | 3.09            | 54                            |
| YZ     | 67.43            | 9.45               | 20.60       | 2.52        | 2.95            | 51                            |
| DF     | 55.38            | 23.20              | 17.07       | 4.35        | 0.70            | 42                            |
| SM     | 58.71            | 28.60              | 3.12        | 9.57        | 0.65            | 38                            |
| XB     | 56.31            | 27.62              | 5.37        | 10.70       | 0.58            | 35                            |

Table 1. Proximate and Vitrinite Reflectance Analyses of Coal Samples
wavenumber range of 4000−400 cm$^{-1}$. The transmission method was adopted in this experiment for infrared spectrum analysis, which required the sample to be mixed with KBr and tableted at pressure of 20 MPa before experiments.

2.3.3. High-Pressure Adsorption Isotherms. The CH$_4$ adsorption experiments were carried out in the pressure range of 0 to 9 MPa and the temperature range of 273 to 373 K, with an interval of 20 K. The high-pressure adsorption instrument (isorb-HP1, US) produced by Quantachrome Corporation was used, and carbon-based materials were degassed under the high vacuum condition at 60 °C for 8 h to remove the impurity gas adsorbed in the coal particles before the tests. For each measurement, approximately 1.5 ∼ 2.0 g of coal and 0.2−0.3 g of activated carbons were weighed. The gas purity specifications were methane (99.999%).

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis of Coal-Based Activated Carbons. The FTIR spectra of raw coal, the carbonization precursor, and coal-based activated carbon are shown in Figure 3. On the whole, the carbonization and activation process greatly changed the molecular structure of raw coal, and a large number of organic functional groups disappeared. Generally, due to the extremely complex structure of coal, the absorption peaks of specific molecular structures in the FTIR spectrum overlap, which makes it difficult to obtain detailed molecular structures directly from the FTIR spectrum. Thus, it is necessary to divide the original FTIR spectrum through the second derivative method to obtain more detailed peak position and peak area data. Absorption bands are usually divided into four regions according to the wavenumber for peak fitting: aromatic structures (700−900 cm$^{-1}$), oxygen-containing structures (1000−1800 cm$^{-1}$), aliphatic structures (2800−3000 cm$^{-1}$), and hydroxyl structures (3000−3800 cm$^{-1}$). The fitted curves of original FTIR spectra were obtained, as shown in Figure 4, and it can be seen that after one-step activation, a large number of complex chemical functional groups on the surface of the coal structure disappeared.

3.1.1. Aromatic Structure Evolution (700−900 Cm$^{-1}$). The out-of-plane flexural vibration of various substituted aromatic hydrocarbons results in absorption peaks in the range of 700−900 cm$^{-1}$. According to the fitting results, the absorption peaks around 745, 800, 827, and 870 cm$^{-1}$ belong to the −CH$^-$ vibration in the substituted aromatic hydrocarbons. By comparing the vibration absorption peaks of substituted aromatic hydrocarbons of raw coal, the carbonized precursor, and activated carbon, it was found that these absorption peaks in the carbonized precursor and activated carbon almost disappeared, indicating that the thermal ablation in the carbonization process caused a large number of substituted −CH$^-$ on the aromatic ring side chain of raw coal to be broken to form the carbonized precursor with a certain strength. In addition, the FTIR spectrum of the raw coal shows the symmetric stretching vibration peak of Si−O and the stretching vibration peak of Si−Cl, which, respectively, appeared at 470 and 540 cm$^{-1}$, as shown in Figure 4. The absorption peaks at these two positions in the carbonized precursor and activated carbon disappeared, indicating that the silicide in the raw coal was removed by the reaction with KOH in the carbonization process, forming the initial pore structure.
3.1.2. Oxygen-Containing Structure Evolution (1000–1800 cm\(^{-1}\)). The absorption peak at the 1600 cm\(^{-1}\) belongs to the aromatic C=C, and its content gradually decreased in the carbonization and activation process, indicating that the destruction of the aromatic ring skeleton structure of raw coal by KOH is carried out throughout the preparation process of activated carbon, especially the activation process. The absorption peaks around 1110, 1230, and 1330 cm\(^{-1}\) were assigned to the stretching vibration of the –C=O bonds of the carboxylic acid, phenol, and alcohol structures, which also showed a decreasing trend, indicating that macromolecular active oxygen-containing functional groups on the surface of raw coal could be effectively removed in the carbonization process. It is worth noting that the FTIR spectra of raw coals GHS, YZ, and DFS showed a strong absorption peak around 1040 cm\(^{-1}\), which is attributed to Si–O–Si/Si–O–C and consistent with the proximate analysis results of coal samples in Table 1. (The ash content of the raw coals GHS, YZ, and DFS is higher.) The disappearance of the strong absorption peak at this position in the carbonized precursor also indicated that ablation of KOH at 500 °C has the effect of removing ash from raw coal.

3.1.3. Aliphatic Structure Evolution (2800–3000 cm\(^{-1}\)). The bands in the range of 2950–2975 cm\(^{-1}\) and 2915–2935 cm\(^{-1}\) are attributed to asymmetric stretching vibration of aliphatic methyl –CH\(_3\) and methylene –CH\(_2\)-, respectively. Meanwhile, the bands in the range of 2860–2875 cm\(^{-1}\) and 2840–2860 cm\(^{-1}\) are attributed to the symmetric stretching vibration of aliphatic methyl –CH\(_3\) and methylene –CH\(_2\)-, respectively. From Figure 4, the contents of aliphatic structures in the high metamorphic anthracite GHS and YZ are less, while the contents in the low metamorphic bituminous coal DFS, SM, and XB are more. However, after ablation by KOH, the aliphatic side chain structure almost disappeared, because it was more easily destroyed than the aromatic ring double bond functional group structure in the carbonization process, and transformed into volatile fractions, which separated from the coal.

3.1.4. Hydroxyl Structure Evolution (3000–3800 cm\(^{-1}\)). The absorption peaks in the band above 3600 cm\(^{-1}\) are due to the stretching vibration of the free hydroxyl group –OH. The associative –OH in the carboxyl (–COOH), alcohol (R–OH), and phenol (Ar–OH) can be observed in the range of 3200–3550 cm\(^{-1}\). The carbonization and activation processes had less effect on the hydroxyl content of the sample, and the processes were effective for the moisture removal of coal samples. It can also be seen from Figure 4 that the proportion of associative –OH in the prepared carbonized precursor and coal-based activated carbons is the highest (semi-quantitative analysis results show that the proportion can account for about 60%), indicating that the KOH thermal ablation transforms complex macromolecular oxygen-containing functional groups
and aliphatic chain structures into relatively simple hydroxyl structures. Therefore, the chemical structure of the coal sample became relatively simple after being prepared as activated carbon, and the pore structure may have a greater impact on the gas adsorption.

3.2. Pore Structure Analysis Based on Low-Temperature Nitrogen Adsorption. The pore structure of materials plays a decisive role in gas storage and separation. Generally, it is believed that the larger the specific surface area and pore volume of the material, the stronger the adsorption capacity of the gas. \( \text{N}_2 \) adsorption–desorption isotherms of coal, the carbonized precursor, and coal-based activated carbon are shown in Figure 5. It can be seen from the comparison that the low-temperature \( \text{N}_2 \) adsorption and desorption isotherms of raw coal are obviously different from those of the carbonized precursor and activated carbon. A large hysteresis loop appears between the adsorption and desorption isotherms in raw coal. This phenomenon occurs because capillary condensation occurs in the mesopores and macropores of the adsorbent surface as the pressure increases. When the relative pressure is less than 0.5, the capillary condensation phenomenon cannot occur, so the adsorption hysteresis phenomenon disappears.

Figure 4. FTIR spectra of raw coal, the carbonization precursor, and coal-based activated carbon.
but the special pore structure in the coal would also make the gas difficult to remove. In contrast, after the carbonization and activation, the adsorption hysteresis almost completely disappeared, indicating that the thermal ablation of the coal body is very serious during the carbonization process. The originally semi-closed pores represented by the ink bottle structure in the coal continued to expand, while the completely closed pores in the coal gradually transformed into open pores.
and some new pores are formed on the previously smooth surface of the coal body by thermal ablation. The activation process includes further thermal ablation of the pores formed during the carbonization process by metallic potassium vapor. The pore structure parameters, such as the specific surface area, pore volume, and pore diameter of all samples are shown in Figure 6, and the PSDs of the samples are shown in Figure 7. The specific surface area and pore volume of raw coal are insignificant compared to those of the carbonized precursor and activated carbon, which differ by 2 orders of magnitude. The specific surface area of coal samples increased from 5.9–18.6 m²/g to 1539.4–1914.3 m²/g for the carbonized
precursor and then to $317.16-3501.4$ m$^2$/g for the activated carbon. The total pore volume of coal samples increased from $0.014-0.025$ cm$^3$/g to $2.691-3.085$ cm$^3$/g for the carbonized precursor and then to $1.746-2.087$ cm$^3$/g for the activated carbon. The micropore volume of coal samples increased from $4.86-9.29 \times 10^{-3}$ cm$^3$/g to $0.543-0.698$ cm$^3$/g for the carbonized precursor and then to $0.543-0.698$ cm$^3$/g for the activated carbon. Previous studies have also found that the temperature and KOH/coal ratio have a great influence on the specific surface area of activated carbon. The higher the KOH/coal ratio, the greater the specific surface area of activated carbon. However, the yield of activated carbon also decreases with the increase of the KOH/coal ratio and also increases the consumption of raw materials. At the same time, with the increase of activation temperature, the specific surface area of activated carbon increases gradually. When the temperature exceeds $800 \degree C$, the specific surface area of activated carbon begins to decrease. During activation, the content of $\cdot \cdot \cdot OH$ also increased with the increase in the KOH content, which contributed to the release of more volatile fractions at high temperatures and the development of more pores. Meanwhile, the pore structures of activated carbon samples prepared by different types of activators were also compared through previous studies. KOH is the most effective activator because of the highest molar content of the metal K per unit mass. The high K content in KOH presumably enabled the generation of more pore structures inside the matrix. By comparison, K$_2$CO$_3$ and KHCO$_3$, despite a low K content, contained more C and O atoms, allowing the generation of more CO$_2$ and water vapor during activation and resulting in larger pore structures and lower specific surface areas.

It can be seen from Figure 7 that the same kind of materials show similar PSDs. The PSD of raw coal is mainly concentrated in the range of micropores around 0.9 nm and the mesopores around 3.4 nm. The PSDs of the prepared materials are more concentrated and mainly in the micropore range (< 2 nm). It is worth noting that the average proportion of micropores in the total pore volume of samples is similar between the raw coal and the carbonized precursor, which is about 30% for both, while the proportion in the activated carbon is increased to about 45%, indicating that although the carbonization process has enriched the pore structure of coal by thermal ablation, it has a pore expansion effect on all the pores in coal. Due to the presence of potassium metal in the activation process, it can regulate the crystal structure of the carbonized precursor and directly generate a large number of micropores. Although more pores are generated in the carbonization process, the activation process is also essential, which is more conducive to the generation of micropores and consistent with the change trend of the average pore diameter in Figure 6d.

### 3.3. High-Pressure Methane and Nitrogen Adsorption

Based on the static adsorption capacity method, the adsorption isotherms of the material were experimentally measured, as shown in Figure 8. It can be seen that the adsorption capacity of coal-based activated carbon for CH$_4$ after preparation is much higher than that of raw coal, and the CH$_4$ adsorption capacity of the carbonized precursor is also between those of raw coal and activated carbon. Compared with previous studies, the adsorption capacity of activated carbon for CH$_4$ is similar under similar conditions. Under high pressure conditions (5 MPa), the CH$_4$ adsorption capacity could reach about 12 mmol/g, indicating that the activity prepared in this study is very efficient.

To obtain characteristic parameters of the adsorption process, such as the ultimate adsorption capacity, curve fitting is required for the data points measured in the experiments. The classical Langmuir model is widely used for isotherm fitting of carbon-based materials:

$$n = \frac{q_m \cdot b \cdot P}{1 + b \cdot P}$$

where $n$ is the adsorption capacity of the adsorbed gas (mmol/g); $P$ is the equilibrium pressure (MPa); $q_m$ is the ultimate adsorption capacity of the adsorbed gas when the adsorption
pressure is infinite (mmol/g); and \( b \) is the adsorption constant (Mpa\(^{-1}\)).

In Figure 9, the adsorption characteristic parameters of different coal samples and their prepared carbonized precursor and activated carbon were compared. After carbonization and activation, the adsorption capacity of raw coal for CH\(_4\) increases continuously, which is consistent with the change trend of micropore volume in synthetic materials. With the increase in temperature, the ultimate adsorption capacity of all samples shows a monotonic decrease. Meanwhile, the adsorption constant \( b \) also reflects the strength of adsorption capacity. Since the adsorption process is exothermic, high temperature is not conducive to the gas adsorption. Therefore, the adsorption constant \( b \) of the carbonized precursor and activated carbon also decreases with the increase in temperature. However, due to the complexity of semi-closed pores in raw coal, the adsorption constant \( b \) obtained by fitting shows an irregular trend of change. In contrast, after the pores of the precursor and activated carbon were expanded by thermal ablation, the connectivity and openness of the pores were better.

### 3.4. Mean Isosteric Heat of Adsorption

The isosteric heat of adsorption is the change of enthalpy at the moment in the adsorption process.\(^{50}\) In order to comprehensively consider

![Figure 10. Relationship between ln(P/n) and n at different temperatures (samples YZ and SM as the example).](image1)

![Figure 11. Relationship between ln(K') and 1/T (samples YZ and SM as the example).](image2)
the affinity of the adsorbent for the gas, the mean isosteric heat of adsorption is used. In Figure 8, linear relationships were observed between the adsorption capacity of the adsorbent and the adsorption equilibrium pressure under low pressure conditions, which is in line with Henry’s law:

\[ n = K'P \]  

(2)

where \( n \) is the adsorption capacity, \( K' \) is Henry’s coefficient, and \( P \) is the adsorption equilibrium pressure.

According to the Clausius–Clapeyron equation, the isosteric heat of adsorption \( q_{st} \) can be calculated by integrating the equation

\[ \left( \frac{d\ln P}{dT} \right)_n = \frac{q_{st}}{RT} \]  

(3)

where \( R \) is the ideal gas constant, 8.314 J/(mol·K), \( T \) is the temperature (K), and \( P \) is the equilibrium pressure (MPa).

The relationship between \( K' \) and temperature \( T \) is obtained by combining eqs 2 and 3:

\[ \frac{d\ln K'}{dT} = \frac{\Delta H_0}{RT^2} \]  

(4)

Thus, it is necessary to first calculate the Henry’s coefficient \( K' \) at different temperatures to obtain the mean isosteric heat of adsorption \( \Delta H_0 \). When the adsorption capacity \( n \) is low, the relationship between \( n \) and \( P \) can be calculated by the virial equation:

\[ \ln(K') = \ln\left( \frac{P}{n} \right) = -A_0 - A_1n \]  

(5)

From eq 5, it can be seen that the slope \( A_1 \) and intercept \( A_0 \) can be obtained through the linear fitting result between \( \ln(P/n) \) and \( n \). The relationship between \( \ln(P/n) \) and \( n \) at different temperatures are shown in Figure 10. The first virial coefficient \( A_0 \) is related to Henry’s coefficient

\[ K' = \exp(A_0) \]  

(6)

By integrating eq 4, the linear relationship between \( \ln(K') \) and \( 1/T \) can be also obtained, as shown in Figure 11. The mean isosteric heat of adsorption can be calculated from the slope obtained by linear fitting, as shown in Table 2. The mean isosteric heat of adsorption calculated in the abovementioned way is independent of temperature and represents the energy released per mole of the gas adsorbed by the adsorbent. In the exothermic adsorption process, the gas molecules transform from three-dimensional motion in free space to two-dimensional motion on the surface of the adsorbent, and their kinetic energy is converted to the outside world in the form of thermal energy. The higher the magnitude of heat released is, the higher the kinetic energy is that the gas molecules lose and the more stable the molecules are on the adsorbent surface. Therefore, the higher the adsorption heat, the stronger the affinity between the adsorbent and the gas molecule. It can be seen from Table 2 that after the preparation of activated carbon, the mean isosteric heat of adsorption of some samples even decreased slightly, indicating that the mean isosteric heat of adsorption is not significantly related to the development degree of the pore structure of the adsorbent. Meanwhile, as the carbon-based porous media are of the same type, the types of surface functional groups of all samples are relatively similar, and it is difficult to cause a great impact on the mean isosteric heat of adsorption. However, due to the adsorption capacity of the prepared activated carbon being far more than that of raw coal, the activated carbon needs to release more heat in the adsorption process as the same equilibrium pressure increased. Thus, the adsorption process is more sensitive to temperature changes. It can also be seen from Figure 9 that with the increase of temperature, the decreasing trend of the ultimate CH₄ adsorption capacity of activated carbon is greater than that of the raw coal and carbonized precursor, which provides a certain guiding significance for the TSA and PSA.

### Table 2. Mean Isosteric Heat of Adsorption (\( \Delta H_0 \)) of Raw Coal, the Carbonization Precursor, and Coal-Based Activated Carbon

| Sample   | \( \Delta H_0 \) (kJ/mol) | Sample   | \( \Delta H_0 \) (kJ/mol) | Sample   | \( \Delta H_0 \) (kJ/mol) |
|----------|---------------------------|----------|---------------------------|----------|---------------------------|
| GHS-Coal | 10.15                     | GHS-T500 | 21.03                     | GHS-AC   | 18.88                     |
| YZ-Coal  | 17.01                     | YZ-T500  | 19.91                     | YZ-AC    | 16.77                     |
| DF-Coal  | 18.93                     | DF-T500  | 20.56                     | DF-AC    | 15.83                     |
| SM-Coal  | 17.51                     | SM-T500  | 19.69                     | SM-AC    | 16.36                     |
| XB-Coal  | 18.65                     | XB-T500  | 18.97                     | XB-AC    | 16.18                     |

4. CONCLUSIONS

In this study, five kinds of anthracite and bituminous coal were used as the raw material for the preparation of a series of carbonization precursors and coal-based activated carbons by the KOH chemical activation method, and the FTIR spectroscopy, low-temperature nitrogen adsorption, and high-pressure adsorption experiments were carried out to obtain the physicochemical structure and adsorption performance of the samples. The main results of the present research work can be summarized as follows:

1. The chemical structure of the coal sample became relatively simple after being prepared as activated carbon. The carbonization and activation process greatly changed the molecular structure of raw coal, and a large number of organic functional groups disappeared. KOH thermal ablation transforms complex macromolecular oxygen-containing functional groups and aliphatic chain structures into relatively simple hydroxyl structures.

2. A large number of pores mainly in the micropore range (< 2 nm) are generated during the carbonization and activation process. The carbonization process has enriched the pore structure of coal by thermal ablation, while activation process is more conducive to the micropores generated. Originally semi-closed pore expansion in the carbonization process results in adsorption hysteresis almost completely disappearing, which is beneficial to the gas adsorption and desorption.

3. The formation of a large number of micropores, especially during the activation process, greatly increases the adsorption capacity of the sample for CH₄. The calculated mean isosteric heat of adsorption being independent of temperature and the development degree of the pore structure shows that the adsorption process of activated carbon is more sensitive to temperature changes, which is consistent with the change trend of ultimate CH₄ adsorption capacity of activated carbon.
AUTHOR INFORMATION

Corresponding Author
Shanshan Li – Institute of Energy, Hefei Comprehensive National Science Center, Anhui, Hefei 230031, China; Joint National-Local Engineering Research Centre for Safe and Precise Coal Mining, Anhui University of Science and Technology, Huainan, Anhui 232001, China; Key Laboratory of Industrial Dust Prevention and Control & Occupational Health and Safety, Ministry of Education and School of Economics and Management, Anhui University of Science and Technology, Huainan, Anhui 232001, China; Email: shanshanli0809@163.com

Authors
Yuanan Zheng – Joint National-Local Engineering Research Centre for Safe and Precise Coal Mining, Anhui University of Science and Technology, Huainan, Anhui 232001, China; Key Laboratory of Industrial Dust Prevention and Control & Occupational Health and Safety, Ministry of Education and School of Safety Science and Engineering, Anhui University of Science and Technology, Huainan, Anhui 232001, China; State Key Laboratory of Deep Coal Mining & Environment Protection, Huainan Mining (Group) Co., Ltd., Huainan, Anhui 232000, China; orcid.org/0000-0002-8405-1619

Bingyou Jiang – Joint National-Local Engineering Research Centre for Safe and Precise Coal Mining, Anhui University of Science and Technology, Huainan, Anhui 232001, China; Key Laboratory of Industrial Dust Prevention and Control & Occupational Health and Safety, Ministry of Education and School of Safety Science and Engineering, Anhui University of Science and Technology, Huainan, Anhui 232001, China; State Key Laboratory of Deep Coal Mining & Environment Protection, Huainan Mining (Group) Co., Ltd., Huainan, Anhui 232000, China

Guofeng Yu – State Key Laboratory of Deep Coal Mining & Environment Protection, Huainan Mining (Group) Co., Ltd., Huainan, Anhui 232000, China; Key Laboratory of Coupled Hazards Prevention and Control in Deep Coal Mining, National Mine Safety Administration, Huaihai Energy Holding Group Co., Ltd., Huainan, Anhui 232000, China

Bo Ren – State Key Laboratory of Deep Coal Mining & Environment Protection, Huainan Mining (Group) Co., Ltd., Huainan, Anhui 232000, China; Key Laboratory of Coupled Hazards Prevention and Control in Deep Coal Mining, National Mine Safety Administration, Huaihai Energy Holding Group Co., Ltd., Huainan, Anhui 232000, China

Haotian Zheng – School of Safety Science and Engineering, Anhui University of Science and Technology, Huainan, Anhui 232001, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c05557

Notes
The authors declare no competing financial interest.

Acknowledgments
Financial supports from the University-level key projects of the Anhui University of Science and Technology (no. xzd2020-01), the Institute of Energy, Hefei Comprehensive National Science Center (no. 21KZS218), the National Natural Science Foundation of China (no. 52104179), the Natural Science Foundation of Anhui Province (no. 2208085QG225), the Independent Research fund of Joint National-Local Engineering Research Centre for Safe and Precise Coal Mining (Anhui University of Science and Technology) (no. EC2021009, EC2022014), the Independent Research Fund of Key Laboratory of Industrial Dust Prevention and Control and Occupational Health and Safety, Ministry of Education (Anhui University of Science and Technology) (no. EK20211004), the Anhui Provincial Key Research Base of Humanities and Social Sciences for Safety Management of Mining Enterprises (no. MF2022004), and the Research Fund of The State Key Laboratory of Deep Coal Mining and Environment Protection (no. SKLDCMEP22KF01) are sincerely acknowledged.

REFERENCES

(1) Li, M.; Lu, Y.; Shi, S.; Li, H.; Tian, Z.; Ye, Q.; Lu, J. Piezoelectric effect and ignition properties of coal mine roof sandstone deformation and fracture. Fuel 2021, 290, 120007.

(2) Kong, X.; Li, S.; Wang, E.; Ji, P.; Wang, X.; Shuang, H.; Zhou, Y. Dynamics behaviour of gas-bearing coal subjected to SHPB tests. Composite Structures 2021, 256, 113088.

(3) Kong, X.; Li, S.; Wang, E.; Wang, X.; Zhou, Y.; Ji, P.; Shuang, H.; Li, S.; Wei, Z. Experimental and numerical investigations on dynamic mechanical responses and failure process of gas-bearing coal under impact load. Soil Dynam. Earthq. Eng. 2021, 142, 106579.

(4) Liu, T.; Lin, B.; Fu, X.; Gao, Y.; Kong, J.; Zhao, Y.; Song, H. Experimental study on gas diffusion dynamics in fractured coal: A better understanding of gas migration in in-situ coal seam. Energy 2020, 195, 117005.

(5) Li, H.; Zheng, C.; Lu, J.; Tian, L.; Lu, Y.; Ye, Q.; Luo, W.; Zhu, X. Drying kinetics of coal under microwave irradiation based on a coupled electromagnetic, heat transfer and multiphase porous media model. Fuel 2019, 256, 115966.

(6) Qin, L.; Ma, C.; Li, S.; Lin, H.; Wang, P.; Long, H.; Yang, D. Mechanical damage mechanism of frozen coal subjected to liquid nitrogen freezing. Fuel 2022, 309, 122124.

(7) Wang, L.; Liu, S.; Cheng, Y.; Yin, G.; Zhang, D.; Guo, P. Reservoir reconstruction technologies for coalbed methane recovery in deep and multiple seams. Int. J. Min. Sci. Technol. 2017, 27, 277–284.

(8) Dong, K.; Ni, G.; Nie, B.; Xu, Y.; Wang, G.; Sun, L.; Liu, Y. Effect of polyvinyl alcohol/aluminum microparticle expansion agent on porosity and strength of cement-based drilling sealing material. Energy 2021, 224, 119966.

(9) Guanhua, G.; Hui, H.; Baisheng, B.; Yan, Y.; Haoran, H.; Shouqing, S.; Gang, G. Research of wetting selectivity and wetting effect of imidazole ionic liquids on coal. Fuel 2021, 286, 119331.

(10) Zheng, Y.; Li, Q.; Yuan, C.; Tao, Q.; Zhao, Y.; Zhang, G.; Liu, J. Influence of temperature on adsorption selectivity: Coal-based activated carbon for CH4 enrichment from coal mine methane. Powder Technol. 2019, 347, 42–49.

(11) Li, H.; Xu, C.; Ni, G.; Lu, J.; Lu, Y.; Shi, S.; Li, M.; Ye, Q. Spectroscopic (FTIR, 1H NMR) and SEM investigation of physicochemical structure changes of coal subjected to microwave-assisted oxidation stimulation. Fuel 2022, 317, 123473.

(12) Yang, H.; Yin, C.; Jiang, B.; Zhang, D. Optimization and analysis of a VPSA process for N2/CH4 separation. Sep. Purif. Technol. 2014, 134, 232–240.

(13) Ammendola, P.; Raganati, F.; Chirone, R. CO2 adsorption on a fine activated carbon in a sound assisted fluidized bed: Thermodynamics and kinetics. Chem. Eng. J. 2017, 322, 302–313.

(14) Ammendola, P.; Raganati, F.; Chirone, R. Effect of operating conditions on the CO2 recovery from a fine activated carbon by means of TSA in a fluidized bed assisted by acoustic fields. Fuel Process. Technol. 2015, 134, 494–501.

(15) Raganati, F.; Ammendola, P.; Chirone, R. On improving the CO2 recovery efficiency of a conventional TSA process in a sound assisted fluidized bed by separating heating and purging. Sep. Purif. Technol. 2016, 167, 24–31.

(16) Gu, M.; Zhang, B.; Qi, Z.; Liu, Z.; Duan, S.; Du, X.; Xian, X. Effects of pore structure of granular activated carbons on CH4...
enrichment from CH4/N2 by vacuum pressure swing adsorption. Sep. Purif. Technol. 2015, 146, 213–218.

(17) Zacharia, R.; Gomez, L. F.; Chahine, R.; Cossement, D.; Benard, P. Thermodynamics and kinetics of CH4/CO2 binary mixture separation by metal-organic frameworks from isotope exchange and adsorption break-through. Microporous Mesoporous Mater. 2018, 263, 165–172.

(18) Hu, J.; Liu, Y.; Liu, J.; Gu, C.; Wu, D. Effects of incorporated oxygen and sulfur heteroatoms into ligands for CO2/N2 and CO2/CH4 separation in metal-organic frameworks: A molecular simulation study. Fuel 2018, 225, 591–597.

(19) Gargiulo, V.; Alle, M.; Raganati, F.; Lisi, L.; Chironne, R.; Ammendola, P. BTC-based metal-organic frameworks: Correlation between relevant structural features and CO2 adsorption performances. Fuel 2018, 222, 319–326.

(20) Li, S.; Han, K.; Li, J.; Li, M.; Lu, C. Preparation and characterization of super activated carbon produced from sugarcane by KOH activation. Microporous Mesoporous Mater. 2017, 243, 291–300.

(21) Celzard, A.; Albiniaik, A.; Jasienko-Halat, M.; Mareché, J. F.; Furdin, G. Methane storage capacities and pore textures of active carbons undergoing mechanical densification. Carbon 2005, 43, 1990–1999.

(22) Srinivasakannan, C.; Zailani Abu Bakar, M. Production of activated carbon from rubber wood sawdust. Biomass Bioenergy 2004, 27, 89–96.

(23) Ahmad, A. A.; Hameed, B. H. Effect of preparation conditions of activated carbon from bamboo waste for real textile wastewater. J. Hazard. Mater. 2010, 173, 487–493.

(24) Wang, L.; Chen, Z.; Wen, H.; Cai, Z.; He, C.; Wang, Z.; Yan, W. Microwave assisted modification of activated carbons by organic acid ammoniums activation for enhanced adsorption of acd red 18. Powder Technol. 2018, 323, 230–237.

(25) Prah, D.; Kartika, Y.; Indraswati, N.; Ismadji, S. Activated carbon from jackfruit peel waste by H3PO4 chemical activation: Pore structure and surface chemistry characterization. Chem. Eng. J. 2008, 140, 32–42.

(26) Nowicki, P.; Kazmierczak, J.; Pietrzak, R. Comparison of physicochemical and sorption properties of activated carbons prepared by physical and chemical activation of cherry stones. Powder Technol. 2015, 269, 312–319.

(27) Li, K.; Zheng, Z.; Li, Y. Characterization and lead adsorption properties of activated carbons prepared from cotton stalk by one-step H3PO4 activation. J. Hazard. Mater. 2010, 181, 440–447.

(28) Guo, Y.; Rockstraw, D. A. Activated carbons prepared from rice hull by one-step phosphoric acid activation. Microporous Mesoporous Mater. 2007, 100, 12–19.

(29) Budinova, T.; Ekinci, E.; Yardım, F.; Grimm, A.; Björnbom, E.; Minkova, V.; Goranova, M. Characterization and application of activated carbon produced by H3PO4 and water vapor activation. Fuel Process. Technol. 2006, 87, 899–905.

(30) Gargiulo, V.; Alle, M.; Ammendola, P.; Raganati, F.; Chironne, R. CO2 sorption on surface-modified carbonaceous support: Probing the influence of the carbon black microporosity and surface polarity. Appl. Surf. Sci. 2016, 360, 329–357.

(31) Raganati, F.; Alle, M.; Gargiulo, V.; Chironne, R.; Ammendola, P. Isotherms and thermodynamics of CO2 adsorption on a novel carbon-magnetite composite sorbent. Chem. Eng. Res. Des. 2018, 134, 540–552.

(32) Raganati, F.; Ammendola, P.; Chironne, R. Effect of acoustic field on CO2 desorption in a fluidized bed of fine activated carbon. Particuology 2015, 23, 8–15.

(33) Al Bahri, M.; Calvo, L.; Gilarranz, M. A.; Rodríguez, J. J. Diuron Multilayer Adsorption on Activated Carbon from CO2 Activation of Grape Seeds. Chem. Eng. Commun. 2014, 203, 103–113.

(34) Hüttinger, K. J.; Minges, R. Catalytic water vapour gasification of carbon: Importance of melting and wetting behaviour of the ‘catalyst. Fuel 1985, 64, 491–494.

(35) Yao, X.; Xie, Q.; Yang, C.; Zhang, B.; Wan, C.; Cui, S. Additivity of pore structural parameters of granular activated carbons derived from different coals and their blends. Int. J. Min. Sci. Technol. 2016, 26, 661–667.

(36) Li, X.; Xing, W.; Zhuo, S.; Zhou, J.; Li, F.; Qiao, S. Z.; Lu, G. Q. Preparation of capacitor’s electrode from sunflower seed shell. Biosource. Technol. 2011, 102, 1118–1123.

(37) Lillo-Ródenas, M. A.; Cazorla-Amorós, D.; Linares-Solano, A. Understanding chemical reactions between carbons and NaOH and KOH: An insight into the chemical activation mechanism. Carbon 2003, 41, 267–275.

(38) Lillo-Ródenas, M. A.; Cazorla-Amorós, D.; Linares-Solano, A.; Béguin, F.; Climent, C.; Rouzaud, J. N. HRTEM study of activated carbons prepared by alkali hydroxide activation of anthracite. Carbon 2004, 42, 1305–1310.

(39) Lillo-Ródenas, M. A.; Juan-Juan, J.; Cazorla-Amorós, D.; Linares-Solano, A. About reactions occurring during chemical activation with hydroxides. Carbon 2004, 42, 1371–1375.

(40) Brunauer, S.; Emmett, P. H.; Teller, E. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 1938, 60, 309–319.

(41) Barrett, E. P.; Joyner, L. G.; Halenda, P. P. The determination of pore volume and area distributions in porous substances. I. computations from nitrogen isotherms. J. Am. Chem. Soc. 1951, 73, 373–380.

(42) Deboer, H. H.; Linsen, B. G.; van der Plas, T.; Zondervan, G. J. Studies on pore systems in catalysts: VII. Description of the pore dimensions of carbon blacks by the t method. J. Catal. 1965, 4, 649–653.

(43) Lastoskie, C.; Gubbins, K. E.; Quirke, N. Pore size distribution analysis of microporous carbons: a density functional theory approach. J. Phys. Chem. 1993, 97, 4786–4796.

(44) Bora, M.; Tamuly, J.; Maria Benoy, S. M.; Hazarika, S.; Bhattacharya, D.; Sakia, B. K. Highly scalable and environment-friendly conversion of low-grade coal to activated carbon for use as electrode material in symmetric supercapacitor. Fuel 2022, 329, 125385.

(45) Tian, X.; Chen, Z.; Hou, J.; Li, Z. Sustainable utilization method of using coal gasification fine ash to prepare activated carbon for supercapacitor. J. Clean. Prod. 2022, 363, 132524.

(46) Chen, T.; Liu, H.; Bie, R. Temperature rise characteristics of coal-KOH adduct under microwave heating and the properties of resultant activated carbon for catalytic methane decomposition. J. Anal. Appl. Pyrolysis 2020, 145, 104739.

(47) Chen, S.; Zhang, B.; Xia, Y.; Chen, H.; Chen, G.; Tang, S. Influence of mixed alkali on the preparation of edible fungus substrate porous carbon material and its application for the removal of dye. Colloid. Surface. A 2021, 609, 125675.

(48) Yang, Y.; Zhou, J.; Wu, L.; Zhang, Q.; Song, Y. Understanding effects of potassium activator on the porous structure and adsorption performance of bluecake-based porous powder during microwave heating. J. Mol. Liq. 2022, 366, 120249.

(49) Hamyali, H.; Nosratinia, F.; Rashidi, A.; Ardjmand, M. Anthracite coal-derived activated carbon as an effectiveness adsorbent for superior gas adsorption and CO2/N2 and CO2/CH4 selectivity: Experimental and DFT study. Sep. Sci. Technol. 2022, 10, 107007.

(50) Jun, S.; Li, X.; Fu, X.; Xia, Q.; Li, Z. Adsorption Isotherms, Kinetics, and Desorption of 1,2-Dichloroethane on Chromium-Based Metal Organic Framework MIL-101. Sep. Sci. Technol. 2013, 48, 1479–1489.

(51) Tang, X.; Wang, Z.; Rippe, N.; Kang, B.; Yee, G. Adsorption Affinity of Different Types of Coal: Mean Isosteric Heat of Adsorption. Energy Fuels 2015, 29, 3609–3615.

(52) Dunn, P. F.; Thomas, F. O.; Leighton, J. B.; Lv, D. Determination of Henry’s law constant and the diffusion and polytropic coefficients of air in aviation fuel. Fuel 2011, 90, 1257–1263.

(53) Cole, J. H.; Everett, D. H.; Marshall, C. T.; Paniego, A. R.; Powl, J. C.; Rodríguez-Reinoso, F. Thermodynamics of the high temperature adsorption of some permanent gases by porous carbons. J. Chem. Soc., Faraday Trans. 1 1974, 70, 2154–2169.
(54) Zhao, X. B.; Xiao, B.; Fletcher, A. J.; Thomas, K. M. Hydrogen adsorption on functionalized nanoporous activated carbons. *J. Phys. Chem. B* 2005, 109, 8880–8888.

(55) Galaon, T.; David, V. Deviation from van’t Hoff dependence in RP-LC induced by tautomic interconversion observed for four compounds. *J. Sep. Sci.* 2011, 34, 1423–1428.