A Study on the Effect of Coal Metamorphism on the Adsorption Characteristics of a Binary Component System: CO$_2$ and N$_2$

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ABSTRACT: At present, there is little research on the multi-component gas adsorption characteristics of coal with different metamorphisms. In this study, DH (low metamorphism), FGZ (medium metamorphism), and DSC (high metamorphism) coal samples were selected as the microscopic research objects, and the molecular models of them were constructed by means of elemental analysis, $^{13}$C NMR, and X-ray. The adsorption characteristics of coal with different metamorphisms under the binary component system (CO$_2$ and N$_2$) were explored by experiments and simulations at 298 K and 1000 kPa. The results showed that in the binary component system gas environment, the adsorption strength of CO$_2$ is stronger than that of N$_2$. DH has the highest isosteric heat of adsorption, and the adsorption strengths of CO$_2$ and N$_2$ is stronger than that for FGZ and DSC. The adsorption amounts of CO$_2$ and N$_2$ by three coal molecules are ranked as DH > FGZ > DSC. The sequence of adsorption selectivity of CO$_2$/N$_2$ is DH > FGZ > DSC > 1, which demonstrates the stronger competitiveness of CO$_2$ than N$_2$. The adsorption selectivity of CO$_2$/N$_2$ for DH is stronger than that for DSC. However, with the increase of the CO$_2$ component, the adsorption selectivity of CO$_2$/N$_2$ for DH has a great influence, while DSC is relatively stable. The simulation results display a good agreement with the experimental results. The research can improve the accuracy and efficiency of inert injection measures and has guiding significance for the prevention and control of coal spontaneous combustion accidents by inert injection.

1. INTRODUCTION

Coal is widely used as a kind of primary fossil fuel and a chemical raw material all over the world. However, the coal spontaneous combustion easily leads to fire disasters during coal production, transportation, and utilization, which causes serious resource waste, environmental pollution, and is even threatening to workers’ lives and health. For nearly half a century, coal chemistry scholars at home and abroad have been devoted to exploring the molecular structure properties of coal from a microscopic perspective, which not only provides a methodological basis for the understanding of the nature of coal but also has important significance for the study of the spontaneous combustion characteristics of coal.

Different from other macromolecular organic matters, coal has no unified physical and chemical structural forms, so the compositions and structures and morphological structures of coal molecules with different metamorphism degrees vary significantly. According to the coal metamorphism degree from low to high, coal can be divided into three categories: lignite, bituminous coal, and anthracite. Researchers analyze the molecular structure changes of coal by a variety of chemical experiments, such as pyrolysis, polycondensation, etc., and explore the effect of small molecular structure products produced by splitting decomposition on the changes of coal molecular structure characteristics, to obtain the molecular structure of coal by inverse deduction. Through continuous improvement and development, the coal molecular structure model has successively gone through the stages of the Fuchs model, Given model, Wiser model, and Shinn model. In the present period, modern techniques, such as X-ray, Raman spectroscopy, high-resolution transmission electron microscopy (HRTEM), $^{13}$C NMR, and so on, are often used for research and analysis. Lian et al. based on X-ray photoelectron spectroscopy, $^{13}$C NMR, and ultimate analysis and constructed the molecular model of the DMC scaffold (DMC-S). Wu et al. used XRD, FTIR, $^{13}$C NMR, SEM, and AFM techniques.
In the study of gas adsorption, CO\textsubscript{2}, N\textsubscript{2}, CH\textsubscript{4} and other mixed gases are mostly studied. Wu et al.\textsuperscript{17} took bituminous coal as the research object, and under the conditions of 298.15–318.15 K and up to 10,000 kPa, he carried out the grand regular Monte Carlo and molecular dynamics simulations for the single, binary, and ternary component systems of CO\textsubscript{2}, N\textsubscript{2}, and O\textsubscript{2}. Wu et al.\textsuperscript{18} studied the ignition characteristics of bituminous coal under the conditions of O\textsubscript{2}/N\textsubscript{2} and O\textsubscript{2}/CO\textsubscript{2} atmospheres. Gao et al.\textsuperscript{20} studied the adsorption characteristics of CH\textsubscript{4}, CO\textsubscript{2}, N\textsubscript{2}, and H\textsubscript{2}O for lignite. Zhao et al.\textsuperscript{21} studied the molecular simulation of adsorption characteristics of CH\textsubscript{4}, CO\textsubscript{2}, and N\textsubscript{2} multicomponent gases in coal and the influence of gas adsorption on coal spontaneous combustion. Zheng et al.\textsuperscript{22} studied the multicomponent gases’ competitive adsorption properties and its effects on the coal oxidations, which were investigated by a gas adsorption analyzer and in situ FTIR spectroscopy. Gao et al.\textsuperscript{23} studied the synergistic mechanism of CO\textsubscript{2} and active functional groups during the low temperature oxidation of lignite. Meng et al.\textsuperscript{29} used the method of combining GCMC and DFT to study the adsorption mechanism of coal methane with the unit structure of coal was very important to the accuracy of methane content through the simulation of methane adsorption on different rank coals. The structure of the supermonomer indicates the degree of coal metamorphism and has a great influence on the adsorption of methane in coal.

The above studies mainly focus on the multicomponent gas adsorption of a single type of coal, while the multicomponent gas adsorption characteristics of coal with different metamorphisms are rarely mentioned, and there is a lack of targeted measures for the prevention and control of spontaneous combustion of different types of coal. In order to explore the microscopic mechanism of inert gas prevention and control of coal spontaneous combustion accidents and improve the accuracy and efficiency of inert gas measures, lignite from Danhou mine, bituminous coal from Fangezhuang mine, and anthracite from Dashucun mine were selected as the research objects in this manuscript. Elemental analysis and 13C NMR and X-ray detection methods were adopted to analyze and study coal samples and build a molecular structure model. By using molecular mechanics (MM) and molecular dynamics (MD) simulations and then the accuracy of simulation is verified by experiments, the adsorption characteristics of coal with different metamorphisms under CO\textsubscript{2} and N\textsubscript{2} binary component system environments were explored from a microscopic perspective.

2. RESULTS AND DISCUSSION

2.1. Molecular Structure Modeling and Optimization.

2.1.1. Test Results of the Total Elemental Analysis. After the experiment, the elemental analysis results are shown in Table 1. In order to obtain more accurate elemental analysis results, the samples were tested for elements C, H, N, S, and O, respectively. The relative content values of the listed elements were determined by experiments instead of the common subtraction method.

2.1.2. Result Analysis of the Nuclear Magnetic Resonance Carbon Spectra (13C NMR) Test. From the results of nuclear magnetic resonance carbon spectra (13C NMR) tests of DH, FGZ, and DSC, it can be seen that the main chemical shifts of DH and FGZ samples appear at 0–70 × 10\textsuperscript{-6}, 100–170 × 10\textsuperscript{-6}, and 210–250 × 10\textsuperscript{-6}, and the main chemical shifts of DSC appears at 100–150 × 10\textsuperscript{-6} as shown in Figure 1.

Due to the complexity of the coal structure and the limitation of nuclear magnetic resonance technology, it is necessary to split the peaks of the spectra to obtain more detailed structure information. The 13C NMR carbon spectrum of coal samples is used for the peak splitting operation, and the peak positions was added as completely as possible to ensure a high fitting degree and accuracy so that the result of the peak splitting was more consistent with the experimental results. After the split-peak fitting operation, data analysis is performed on the results, and the structural attribution is determined according to the chemical shift value; then, the relative area value of each coal sample structure is used to calculate the 12 structure parameters of the coal sample, as shown in Table 2.

According to the value of structural parameters, the important parameter $X_{BP}$ of the macromolecular structure can be calculated, namely, the ratio of aromaticity bridge carbon to perimeter carbon. This parameter reflects the average value of the degree of condensation of aromatic rings in the coal structure. $X_{BP} = \frac{I_a}{I_P + I_a + I_s}$. According to the formula, the $X_{BP}$ of DH is 0.49, the $X_{BP}$ of FGZ is 0.28, and the $X_{BP}$ of DSC is 0.11.

2.1.3. Result Analysis of the X-ray Photoelectron Spectroscopy (XPS) Test. The results of X-ray photoelectron spectroscopy (XPS) of DH, FGZ, and DSC show that different peak positions correspond to different existing states of an element. As shown in Tables 3–5, the corresponding structural attribution and proportion of the elements were obtained from the split-peak fitting operation for each element.

| name | weight (mg) | C (%) | H (%) | O (%) | N (%) | S (%) |
|------|-------------|-------|-------|-------|-------|-------|
| DH   | 1.6530      | 58.88 | 4.36  | 25.38 | 0.65  | 0.21  |
| FGZ  | 1.6770      | 80.17 | 4.76  | 4.728 | 1.51  | 1.29  |
| DSC  | 1.8250      | 82.48 | 3.62  | 3.399 | 1.26  | 0.18  |

Table 1. Element Composition of Coal Samples
2.1.4. The Establishment of a Coal Macromolecular Structure Model. According to the element, 13C NMR, and XPS detection result analyses, the proportion and quantity of each structure in the coal macromolecular structure can be roughly calculated. The macromolecular structure diagrams are drawn and revised to get the final plan view of the DH, FGZ, and DSC macromolecular structure models. Materials studio 8.0 can be used for structure optimization and annealing simulation, a three-dimensional view of the coal macromolecular structure model after optimization is obtained, as shown in Figure 2.

Figure 1. 13C NMR test carbon spectra and split peak fitting diagram of DH (a), FGZ (b), and DSC (c).

Table 2. Structure Parameters of Coal Samples

| name  | \( f_A \) | \( f_C \) | \( f_\text{C} \) | \( f_\text{N} \) | \( f_\text{N}^\text{aH} \) | \( f_\text{N}^\text{aH}^\text{H} \) | \( f_\text{N}^\text{aH}^\text{H}^\text{H} \) | \( f_\text{N}^\text{aH}^\text{H}^\text{H}^\text{H} \) | \( f_\text{a}^\text{al} \) | \( f_\text{a}^\text{al}^\text{H} \) | \( f_\text{a}^\text{al}^\text{H}^\text{H} \) | \( f_\text{a}^\text{al}^\text{H}^\text{H}^\text{H} \) |
|-------|----------|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| DH    | 60.12    | 0.96     | 59.16           | 36.86           | 22.30           | 7.45            | 9.94            | 19.46           | 39.88           | 13.63           | 19.46           | 6.79            |
| FGZ   | 82.69    | 0.64     | 82.05           | 26.28           | 55.77           | 2.56            | 5.77            | 17.95           | 17.31           | 6.41            | 10.26           | 0.64            |
| DSC   | 98.22    | 1.93     | 96.29           | 19.25           | 77.04           | 0.53            | 9.34            | 9.38            | 1.78            | 0.24            | 0.26            | 1.29            |

\( f_\text{a} \): total aromaticity carbon; \( f_C \): carbonyl group carbon; \( f_\text{C} \): carbon in aromatic nucleus; \( f_\text{N} \): nonprotonated aromaticity carbon; \( f_\text{aH} \): protonated aromaticity carbon; \( f_\text{aH}^\text{H} \): oxygen-linked aromaticity carbon; \( f_\text{aH}^\text{H}^\text{H} \): side branch aromaticity carbon; \( f_\text{aH}^\text{H}^\text{H}^\text{H} \): bridging aromaticity carbon; \( f_\text{aH}^\text{H}^\text{H}^\text{H}^\text{H} \): total aliphatic carbon; \( f_\text{aH}^\text{H}^\text{H}^\text{H}^\text{H}^\text{H} \): methyl carbon or quaternary carbon; \( f_\text{aH}^\text{H}^\text{H}^\text{H}^\text{H}^\text{H}^\text{H} \): methylene carbon; and \( f_\text{aH}^\text{H}^\text{H}^\text{H}^\text{H}^\text{H}^\text{H}^\text{H} \): oxygen-linked aliphatic carbon.

Table 3. Structure Attributions of C, O, and N Atoms in DH

| atom | peak position (BE) | area (P) | relative area (%) | structure attribution       |
|------|--------------------|----------|------------------|----------------------------|
| C    | 283.81             | 17955.22 | 66.85            | C–C                        |
|      | 284.99             | 5584.85  | 20.8             | C–H                        |
|      | 286.25             | 824.32   | 3.07             | C–O                        |
|      | 287.81             | 2491.69  | 9.28             | C=O                        |
|      | 531.13             | 12761.57 | 29.31            | C=O                        |
|      | 531.27             | 12816.36 | 29.44            | C=O                        |
|      | 531.78             | 4710.54  | 10.82            | C=O                        |
|      | 532.55             | 13244.37 | 30.43            | C=O                        |
| N    | 399.22             | 943.18   | 70.88            | pyridinic nitrogen N-6      |
|      | 400.04             | 301.11   | 22.63            | pyridinic nitrogen N-5      |
|      | 401.29             | 50.74    | 3.82             | quaternary nitrogen         |
|      | 402.08             | 35.59    | 2.68             | oxidized nitrogen           |

Table 4. Structure Attributions of C, O, N, and S Atoms in FGZ

| atom | peak position (BE) | area (P) | relative area (%) | structure attribution       |
|------|--------------------|----------|------------------|----------------------------|
| C    | 283.54             | 31776.32 | 70.74            | C–C                        |
|      | 284.45             | 10376.05 | 23.10            | C–H                        |
|      | 287.64             | 1908.42  | 4.25             | C–O                        |
|      | 289.73             | 856.57   | 1.91             | C=O                        |
|      | 531.60             | 7920.54  | 73.25            | C=O                        |
|      | 531.78             | 2538.82  | 23.48            | C=O                        |
|      | 532.29             | 215.63   | 1.99             | C=O                        |
|      | 532.57             | 138.31   | 1.28             | C=O                        |
| N    | 396.99             | 256.79   | 18.60            | pyridinic nitrogen N-6      |
|      | 397.76             | 194.67   | 14.10            | pyridinic nitrogen N-5      |
|      | 398.37             | 354.90   | 25.71            | pyridinic nitrogen N-6      |
|      | 399.04             | 573.99   | 41.59            | pyridinic nitrogen N-5      |
| S    | 163.04             | 680.93   | 100              | thiophene-S                 |
to the lowest energy value is more accurate after exceeding the value. After the simulation, the DH macromolecular model density is 1.15 g/cm³ and the energy is 895.073 kcal/mol, as shown in Figure 3.

2.2. Data Analysis of Adsorption Characteristics. The molecular models of CO₂ and N₂ were drawn in Materials Studio 8.0 software, and both were optimized by using the geometric optimization and energy tasks in the force module. Figure 4 shows the optimized molecular model of CO₂ and N₂, with a C=O bond distance of 1.160 Å and a N≡N bond distance of 1.098 Å, for the adsorption simulation study.

2.2.1. Isosteric Heat of Adsorption. Adsorption heat refers to the direct interaction between the absorbent and the adsorbate, and the heat released in the process of gas adsorption reflects the adsorption strength to some extent.17,31 Figure 5 shows that the isosteric heat of adsorption of CO₂ for DH is about 8.8—9.0 kcal/mol, that for FGZ is about 8.6—8.9 kcal/mol, and that for DSC is about 8.2—8.4 kcal/mol; the isosteric heat of adsorption of N₂ for DH is about 4.5—4.8 kcal/mol, that for FGZ is about 4.2—4.5 kcal/mol, and that for DSC is about 4.4—4.7 kcal/mol. Therefore, the isosteric heat of adsorption of CO₂ > N₂, and the isosteric heat of CO₂ is about twice as much as that of N₂, that is, the adsorption strength of CO₂ is obviously stronger than that of N₂. The isosteric heat of adsorption of CO₂ in the mixed gas environment by three coal molecules are ranked as DH > FGZ > DSC; but that of N₂ are ranked as DH > HD > DSC. It can be seen that the DH lignite with low metamorphism has the strongest adsorption strength for CO₂ and N₂ compared with other two kinds of coal. Because the O contents of DH is much higher than that of FGZ and DSC, as shown in Table 1, the O contents can significantly enhance the isosteric adsorption heat of CO₂ and N₂.32—34

It can be seen from the isosteric heat of adsorption of CO₂ and N₂ in the CO₂/N₂ mixed gas environment for DH, FGZ, and DSC that the minimum value of CO₂/N₂ appears at the CO₂ component that is less than 10%. At this point, the adsorption strength is weak, and the possibility of desorption is greater. When the CO₂ component is greater than 10%, the isosteric heat of adsorption of CO₂/N₂ for the three coal samples generally shows an upward trend. With the increase of the component of CO₂, the adsorption strength of CO₂ and N₂ also increases, and the adsorption becomes more firm, and the possibility of desorption reaction decreases.

2.2.2. Adsorption Amount and Adsorption Selectivity. 2.2.2.1. Adsorption Amount. The adsorption amount simulated by the sorption module in Materials Studio 8.0 software is in the form of the number of adsorbed gas molecules, and the unit is the number of average molecules per cell. Therefore, it is necessary to convert the simulated value into the actual value of a unified unit and introduce the conversion formula,19

\[ A = \frac{a}{M} \times 1000 \]

where \( a \) means the number of adsorption molecules and \( M \) indicates the relative molecular weight of coal molecules, in g/mol; \( A \) is the result of unit conversion, in mmol/g.

The molecular formula of DH is \( C_{215}H_{191}O_{30}N_{40} \), the adsorption amount for DH is 7.03 mmol/g, that for FGZ is 5.67 mmol/g, and that for DSC is 4.95 mmol/g; in the pure N₂ adsorption environment the component of CO₂ is 0%, the adsorption amount for DH is 2.59 mmol/g, that for FGZ is 2.38 mmol/g, and that for DSC is 1.64 mmol/g. The adsorption amounts of CO₂ and N₂ in the mixed gas environment by three coal samples are ranked as DH > FGZ > DSC, which closely agrees with the simulation result from Gao et al.28 that the high metamorphism of coal is negative to the adsorption amounts of CO₂ and N₂. This is contrary to the fact that researchers generally believe that the adsorption amount of coal is positively correlated with the degree of metamorphism.34,35 However, many researchers have found that the coal metamorphism is not linearly related to the adsorption amount.27,28,36,37 According to our research, DH is a lignite with low metamorphism, and its oxygen-containing functional groups (OCFGs) are much higher than that of the other two coal samples. There are more OCFGs, including 2 —C=O, 16 —OH, 1 —COOH, and 5 —C(==O)−O; FGZ is a medium metamorphism bituminous coal, and its molecular structure consists of six —C=O and four —OH; DSC is anthracite with high metamorphism, including two —C=O, two —OH, one —O−, and one —C(==O)−O. The surface

**Table 5. Structure Attributions of C, O, N, and S Atoms in DSC**

| atom | peak position (eV) | area (%) | structure attribution |
|------|------------------|----------|----------------------|
| C    | 283.61           | 3417.28  | 67.64                | C–C                  |
|      | 284.42           | 11660.33 | 25.07                | C–H                  |
|      | 284.94           | 1711.96  | 5.22                 | C–O                  |
|      | 289.18           | 2216.69  | 4.77                 | C==O                 |
| O    | 531.12           | 1639.02  | 12.63                | C–O                  |
|      | 531.73           | 11111.67 | 85.64                | C==O                 |
|      | 535.97           | 224.74   | 1.73                 | COOH                 |
| N    | 397.82           | 1054.98  | 51.25                | N–6                  |
|      | 399.41           | 428.13   | 20.81                | N–5                  |
|      | 401.13           | 105.38   | 5.12                 | N–Q                  |
|      | 401.89           | 76.20    | 3.71                 | N–Q                  |
|      | 402.94           | 392.88   | 19.11                | N–O                  |
| S    | 163.14           | 252.17   | 100                  | thiophene–S          |

**Figure 2.** Macromolecular structure diagram of DH (a), FGZ (b), and DSC (c).
OCFGs can significantly enhance the CO$_2$ and N$_2$ adsorption amount.\textsuperscript{31} As can be seen from the adsorption amount curve, when the component of CO$_2$ is less than 10%, CO$_2$ adsorption is in a state of rapid growth, and N$_2$ adsorption is in a state of rapid decline, and the adsorption amount of N$_2$ is less than 1 mmol/g. When the component of CO$_2$ was divided into 10−60%, the CO$_2$ adsorption showed a slow upward trend, and the N$_2$ adsorption showed a slow downward trend, tending to 0 mmol/g. When the component of CO$_2$ is greater than 60%, the CO$_2$ adsorption tends to be saturated, and the N$_2$ adsorption is close to 0 mmol/g.

In order to ensure the validity of experimental data, error analysis was carried out for each experiment of three kinds of coal samples. The concepts of uncertainty and confidence

![Figure 3. Macromolecular structures of DH (a), FGZ (b), and DSC (c) with their unit cell structures.](image)

![Figure 4. Molecular models of CO$_2$ (a) and N$_2$ (b).](image)

![Figure 5. Isosteric heat of adsorption for DH, FGZ, and DSC at 298 K and 1000 kPa.](image)
interval are introduced. The uncertainty of the measured adsorption amount of CO$_2$/N$_2$ can be estimated as $X_i = X_i^{\text{measured}} \pm \delta X_i$, where $X_i^{\text{measured}}$ is the mean value of the $n$ set of repeated experiments, $\sigma$ is the standard deviation of repeated experiment data. Figure 6b plotted the mean value and error bar of adsorption amount of CO$_2$/N$_2$ after repeated experiments and determined the uncertainty of CO$_2$/N$_2$ measured. The relative uncertainty of the adsorption amount of CO$_2$/N$_2$ measurements is less than 6% ($\pm 2\sigma/T$) with 95% confidence.

The adsorption experiment results showed that the variation trend of the adsorption amount was consistent with the simulation results, as shown in Figure 6; the adsorption amount of CO$_2$ was greater than N$_2$, and the adsorption amount of CO$_2$ and N$_2$ in the mixed gas environment by three coal molecules are also ranked as DH > FGZ > DSC. There are errors between the adsorption amount of experiment and the average adsorption amount from simulation, as shown in Figure 7. The simulation results of the CO$_2$ adsorption amount are generally higher than the experimental results, which may be affected by coal ash. The experimental results of the N$_2$ adsorption amount were higher than the simulated results, which is due to the fact that the N$_2$ adsorption amount was small and tended to be 0 mmol/g after the CO$_2$ component was greater than 20%. Therefore, the experimental instrument accuracy is not enough and the measurement value is relatively large. Meanwhile, the errors may be caused by insufficient adsorption, inaccurate measurements, and improper storage of samples. The mean absolute error (MAE) between experimental and simulated results of CO$_2$ is less than 1.2 and that of N$_2$ is less than 0.15. Therefore, it is feasible to study gas adsorption behavior by constructing coal molecules.

2.2.2.2. Adsorption Selectivity. Adsorption selectivity is a criterion used to assess the performance of a sorbent in preferentially adsorbing one species in a binary mixed atmosphere. The adsorption selectivity, \[ S_{CO_2/N_2} = \frac{x_{CO_2} / y_{CO_2,\text{adsorbed}}}{x_{N_2} / y_{N_2,\text{bulk}}} \] where $x_{CO_2}$ (or $x_{N_2}$) and $y_{CO_2}$ (or $y_{N_2}$) represents the mole fraction of species CO$_2$ (or N$_2$) in the adsorbed phase and bulk phase, respectively. Therefore, the fact that the adsorption selectivity $S_{CO_2/N_2}$ is larger than 1 indicates that the competitive capacity of adsorbate CO$_2$ in the mixed components is stronger than adsorbate N$_2$, and the greater the selectivity, the stronger the adsorption. If the $S_{CO_2/N_2}$ is less than 1, the competitive adsorption capacity of adsorbate N$_2$ is stronger than adsorbate CO$_2$. The $S_{CO_2/N_2}$ is equal to 1, which means that the competitive adsorption capacity of adsorbates CO$_2$ and N$_2$ is equal.

To ascertain the competitive ability of the coal with different metamorphisms for CO$_2$ and N$_2$, the adsorption selectivity is...
In order to study the adsorption characteristics of coal with different metamorphisms in the environment of binary component system gases of $\text{CO}_2$ and $\text{N}_2$, the macromolecular structure models of DH, FGZ, and DSC were constructed by using elemental analysis and $^{13}$C NMR and XPS detection methods. By means of simulation and experiment, the microscopic mechanism of $\text{CO}_2$ and $\text{N}_2$ mixed gases adsorbed by coal with different metamorphisms was explored.

Molecular mechanics (MM) and molecular dynamics (MD) simulations were used to optimize the molecular structure, and GCMM simulation was used to calculate the isosteric heat of adsorption and the adsorption amounts of three kinds of coal samples in the multicomponent gas environment of different proportions at 298 K and 1000 kPa. After comparison and analysis with the experimental values, the following relationships were obtained: (1) For the same coal sample, the adsorption strength of $\text{CO}_2$ is stronger than that of $\text{N}_2$; for different coal samples, the DH with low metamorphism has the highest isosteric heat of adsorption, namely, the strongest adsorption strength for $\text{CO}_2$ and $\text{N}_2$, which is stronger than FGZ and DSC. (2) The adsorption amounts of $\text{CO}_2$ and $\text{N}_2$ from three coal molecules are ranked as DH > FGZ > DSC, indicating that high metamorphism of coal is negative to the adsorption amounts of $\text{CO}_2$ and $\text{N}_2$. (3) The sequence of adsorption selectivity of $\text{CO}_2/N_2$ for DH with a high metamorphic degree is stronger than that for DSC with a high metamorphic degree, indicating that the adsorption selectivity of $\text{CO}_2/N_2$ on the metamorphic degree is negative. After linear fitting of the adsorption selectivity values, the adsorption selectivity of $\text{CO}_2/N_2$ for DH with low metamorphism has a great influence, while DSC with high metamorphism is relatively stable.

According to the experimental results, the adsorption selectivity of $\text{CO}_2/N_2$ is calculated as shown in Figure 8b. The trend and $\text{R}^2$ of the fitted curve of DH, FGZ, and DSC from simulation are similar to the experiment. However, the $S_{\text{CO}_2/N_2}$ of DH ranges from 29 to 41, the $S_{\text{CO}_2/N_2}$ of FGZ is between 40 and 56, and the $S_{\text{CO}_2/N_2}$ of DSC is between 37 and 44; the sequence of $S_{\text{CO}_2/N_2}$ was DH > FGZ > DSC. It can be seen that the adsorption selectivity of $\text{CO}_2/N_2$ for DH with low metamorphic degree is stronger than that for DSC with a high metamorphic degree, indicating that the adsorption selectivity of $\text{CO}_2/N_2$ on the metamorphic degree is negative. After linear fitting of the adsorption selectivity values, the adsorption selectivity of $\text{CO}_2/N_2$ for DH with low metamorphism has a great influence, while DSC with high metamorphism is relatively stable.

To a certain extent, the results of simulation and experiment reveal the adsorption characteristics of coal with different metamorphic degrees in a binary mixed gas environment. In order to study this phenomenon further, we will continue to analyze and summarize more coal samples to obtain more perfect research conclusions.

3. CONCLUSIONS

In order to study the adsorption characteristics of coal with different metamorphisms in the environment of binary mixed gas system gases of $\text{CO}_2$ and $\text{N}_2$, the macromolecular structure models of DH, FGZ, and DSC were constructed by using elemental analysis and $^{13}$C NMR and XPS detection methods. By means of simulation and experiment, the microscopic mechanism of $\text{CO}_2$ and $\text{N}_2$ mixed gases adsorbed by coal with different metamorphisms was explored.

Molecular mechanics (MM) and molecular dynamics (MD) simulations were used to optimize the molecular structure, and GCMM simulation was used to calculate the isosteric heat of adsorption and the adsorption amounts of three kinds of coal samples in the multicomponent gas environment of different proportions at 298 K and 1000 kPa. After comparison and analysis with the experimental values, the following relationships were obtained: (1) For the same coal sample, the adsorption strength of $\text{CO}_2$ is stronger than that of $\text{N}_2$; for different coal samples, the DH with low metamorphism has the highest isosteric heat of adsorption, namely, the strongest adsorption strength for $\text{CO}_2$ and $\text{N}_2$, which is stronger than FGZ and DSC. (2) The adsorption amounts of $\text{CO}_2$ and $\text{N}_2$ from three coal molecules are ranked as DH > FGZ > DSC, indicating that high metamorphism of coal is negative to the adsorption amounts of $\text{CO}_2$ and $\text{N}_2$. (3) The sequence of adsorption selectivity of $\text{CO}_2/N_2$ was DH > FGZ > DSC > 1, which demonstrates the stronger competitiveness of $\text{CO}_2$ than $\text{N}_2$. (4) The adsorption selectivity of $\text{CO}_2/N_2$ for DH with a low metamorphic degree is stronger than that for DSC with a high metamorphic degree. However, with the increase of the $\text{CO}_2$ component, the $\text{CO}_2/N_2$ adsorption selectivity for DH with low metamorphism has a great influence, while DSC with high metamorphism is relatively stable. The research can improve the accuracy and efficiency of inert injection measures and has guiding significance for the prevention and control of coal spontaneous combustion accidents by inert injection.

4. EXPERIMENTAL AND SIMULATION METHODS

4.1. Experimental Methods. 4.1.1. Sample Preparation. Select lignite from Danhou mine (DH), bituminous coal from Fangezhuang mine (FGZ), and anthracite from Dashucun mine (DSC) samples remove respectively the surface part of large fresh coal samples and crush them into 60–80 mesh pulverized coal; use hydrofluoric acid to demineralize the pulverized coal to reduce the influence of minerals in the pulverized coal on the experiment analysis results; then, clean...
the demineralized pulverized coal until the solution becomes neutral; finally, put the pulverized coal into the drying box, and vacuum packaging is carried out immediately after drying for 12 h.

4.1.2. Elemental Analysis. The elemental analysis of the sample is conducted on the basis of the national standard (GB/T 476-2008) to determine the dry mineral—matter free content of elements C, H, N, S, and O in the coal macerals.

4.1.3. Nuclear Magnetic Resonance Carbon Spectra (13C NMR) Test. The nuclear magnetic resonance carbon spectra (13C NMR) are tested on the JNM-ECZ600R spectrometer at the Zhong Ke Bai Ce laboratory; the resonance frequency is 150.91 MHz. Use a 3.2 mm probe to record the spectra at a 15 kHz rotation rate at room temperature. The experiment delay time is 3 s, and the contact time is 2 ms. The number of scans is 2000.

4.1.4. X-ray Photoelectron Spectroscopy (XPS) Test. X-ray photoelectron spectroscopy (XPS) test is performed on a Thermo escalab 250Xi X-ray photoelectron spectrometer (XPS) at the Zhong Ke Bai Ce laboratory. Use a 180° hemispherical energy analyzer, Al target, power of 150 W, 650 μm beam spot, voltage of 14.8 kV, and current of 1.6 A; and use the pollution carbon C1s = 284.8 eV to complete the charge calibration. The common energy for a narrow scan is 20 eV and 100 eV for a wide scan, and the vacuum degree is 1 × 10−10 mbar.

4.1.5. Adsorption Experiments. The principle of the adsorption experiment system is shown in Figure 9, including the vacuum pumping system, the adsorption reaction system, and the data acquisition system. The vacuum pumping system includes a vacuum pump, a vacuum pressure gauge, and an adsorption cylinder; the adsorption reaction system includes a high-pressure gas cylinder, pressure gauge of mixed gas, hose, and adsorption cylinder; the data acquisition system includes an adsorption cylinder, pressure gauge, and a gas chromatograph. Through direct observation, read the pressure difference between the adsorption cylinder and the pressure gauge before and after the adsorption reaction, and calculate the total adsorption amount of the system; the content of each component was determined by gas chromatography.

The pulverized coal is placed in the adsorption tank, because the pressure is proportional to the amount of the material at room temperature. Therefore, the gas pressure ratio is the gas component ratio. The mixed gas was mixed in different proportions and injected into the adsorption cylinder for the adsorption experiment. The experiment lasted for 24 h. The difference value of the pressure gauge and the gas data of each component detected by the gas chromatograph were read to calculate the adsorption amount. It was set that the CO2 group was divided into a group of 0−100% and every interval of 20%. Coal is a known substance whose structure may vary greatly. In order to reduce the experimental error, a total of 18 experiments were carried out on the three kinds of coal samples, each of which was conducted for three times.

4.2. Simulation Methods. 4.2.1. The Establishment of a Coal Molecular Structure Model. We perform the results of nuclear magnetic resonance carbon spectra (13C NMR) and X-ray photoelectron spectroscopy (XPS) to split-peak fitting operation. According to the fitting results, attribution and parameters of the carbon skeleton structure as well as the heteroatom structure attribution are determined, respectively. Then, build a plan view of a coal macromolecular structure model with reference to the test results of elemental analysis, and make the nuclear magnetic resonance carbon spectra (13C NMR) prediction about the plan view drawn. By comparing the predicted spectra with the nuclear magnetic resonance carbon spectra (13C NMR) test, the structural connection position and method are further adjusted to obtain a relatively accurate plan view of the coal macromolecular structure model.

By using the Geometry Optimization task in the Forcite module of Materials Studio 8.0 software to geometrically optimize the coal macromolecular structure model plan view, in which the Dreiding force field is selected, the maximum number of iteration steps is 50,000; annealing kinetics simulation is performed on the optimized model in the previous step to overcome the energy barrier. Select the Anneal task in the Forcite module, and set the simulated temperature to 300−600 K, the heating step to 5, the cycle step to 10,000 steps, and the cycle to 10 times. Set the time step to 1 fs and the temperature to constant with the Nose temperature control. In this way, we can obtain the final optimized coal molecular structure model diagram.

4.2.2. Optimization of a Unit Cell Density Structure. Amorphous Cell module in Materials Studio 8.0 software is used to construct a unit cell structure. Set an initial density value of 0.7 g/cm³, a final density value of 1.4 g/cm³, an interval of 0.05 g/cm³, and a number of molecules of three; thus, periodic boundary conditions are added to coal molecules to explore the optimal geometric structure under periodic boundary conditions.

4.2.3. Grand Canonical Ensemble Monte Carlo (GCMC) Simulation. Use the Fixed pressure task in the Sorption module of Materials Studio 8.0 software to calculate the isothermal and isobaric adsorption simulation processes. The optimized molecular models of DH, FGZ, and DSC are used as adsorbents, and the gas mixture containing CO2 and N2 is used as adsorbent. The simulated temperature is 298 K, the pressure is 1 MPa, and the balance steps and production steps are 10⁶ and 10⁷, respectively; the simulated force field continues to use Dreiding, the charge balance method is QEq, the maximum calculation steps are 5000 steps, and the convergence standard is 5e−4 e; van der waals and electrostatic interactions are calculated based on Atom-based and Ewald and Group methods, respectively, and the cutoff distance is 18.5 Å.

By setting values of different partial pressure ratios and adjusting the composition of gaseous substances, multiple sets of data simulation and comparative analysis of the macromolecular structures of DH, FGZ, and DSC are carried out. The component of CO2 was set as a group from 0 to 100% every 10%, and 1, 5, 95, 99%, and pure N2 were set.
respectively, which means that there were 45 groups of simulation tasks for three kinds of coal samples.

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**Notes**
The authors declare no competing financial interest.

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