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Molecular Simulation Study on the Effect of Co-Associated Minerals on Methane Adsorption and Mechanical Properties of Coal

Xiaoyu Zhang [1], Yingjie Liu [1], Tianbai Zhou [1], Yongbo Cai [1,*] and Bin Zhang [2]

[1] Chinese Institute of Coal Science, Beijing 100013, China; zhangxy@ccteg-bigdata.com (X.Z.); liuyingjie@mail.ccri.ccteg.cn (Y.L.); zhoutb@ccteg-bigdata.com (T.Z.)
[2] Key Laboratory of In-Situ Property Improving Mining of Ministry of Education, Taiyuan University of Technology, Taiyuan 030024, China; zhangbin@tyut.edu.cn
* Correspondence: caiyongbo@mail.ccri.ccteg.cn

Abstract: When rockbursts and coal and gas outbursts simultaneously occur in a coal mine, changes in gas adsorption (concentration of ambient methane) and displacement of coal and rock must occur. The co-associated minerals in coal reservoirs can affect the mechanical properties and methane adsorption capacity, which are commonly disregarded. It is important to construct compound molecular structure models of coal and rock and conduct molecular dynamic simulations to gain a microscopic understanding of underground disasters. In this work, the molecular structure models of anthracite and coking coal–rock compound models containing different contents of calcite and kaolinite were constructed, and the methane adsorption amount and mechanical properties considering temperature, pressure, and mineral contents were simulated and analysed. The results showed that the methane adsorption amount of the compound models increased rapidly, then increased moderately, and stabilized eventually with increasing adsorption pressure, and the Langmuir fitting findings were good. The saturation adsorption amount of methane in the coal models linearly decreased with increasing temperature, while the methane adsorption heat increased. The presence of minerals adsorbed a certain amount of methane, and the methane adsorption amount increased with increasing mineral contents. The mechanical properties of coal molecules changed when mineral molecules such as calcite and kaolinite were present, which had opposite contribution effects. The addition of kaolinite minerals to the coal molecular model always increased the bulk modulus and shear modulus, while the addition of calcite decreased the bulk modulus of the anthracite, causing an increase in the brittleness of the models. The results of the study further explain the adsorption behaviour and mechanical properties of methane in coal and minerals.

Keywords: coal–rock compound molecular structure models; methane adsorption; mechanical properties; coal; mineral matter; coal and gas outburst

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1. Introduction

Since the 21st century, coal mining technology has been greatly upgraded, integrated mining and caving mining methods have been promoted, and the number of rockburst coal mines in China increased to 121 by 2008. With the increasing coal mining intensity and depth in China, the number of mines with rockbursts rapidly increased from 142 in 2012 to 177 in 2017 [1]. The accident investigations revealed that two disasters, a rock burst and a coal and gas outburst, simultaneously occurred. For example, the average mining depth of the Pingdingshan No. 12 Coal Mine reached 1100 m, and the rockburst and coal and gas outbursts occurred on 29 June 2005 and 19 March 2006 [2]. The occurrence mechanism of compound disasters is complex, and the prediction index for a single disaster may be invalid [3]. Research on the mechanism of compound disasters is one of the most fundamental research contents in the study of compound disasters and provides a theoretical

basis for the evaluation, prediction, and prevention of compound disasters [4]. Just like the human gene sequence, the molecular structures determine the thermodynamic, optical, electromagnetic, and surface properties of coal. The mechanism of methane adsorption and mechanical properties can be reflected through molecular dynamic simulation, so varied coal molecular structure models under different geological conditions need to be built urgently, and the effects of pressure, temperature and mineral contents on methane adsorption need to be clarified. To clarify the mechanism of rockbursts, coal and gas outbursts, and the relationship between the two disasters, this study constructs coal–rock compound structure models, which are intended to provide a reference for the dynamic mechanism of compound disasters.

Analysis and interpretation of the occurrence mechanism of rockburst include strength theory [5], stiffness theory [6], energy theory [7], impact propensity theory [8], "three criteria" theory [9], deformation system instability theory [10], and "three factors" theory [11]. There are three important factors in the occurrence of a rockburst hazard, the propensity to impact is the intrinsic factor, the high-stress concentration and dynamic disturbance is the source factor, and the presence of soft layers in the coal rock is the structural factor. Qi et al. pointed out that a coal rock structure with impact tendency deforms under the action of high stress, forming a high-stress concentration and locally gathering energy. Under the disturbance of mining stress, stick–slip and the release of a large amount of energy along the weak surface or contact surface of the coal rock structure will cause a rockburst disaster [12]. Analysis and interpretation of the occurrence mechanism of coal and gas outbursts include the comprehensive action hypothesis [13], rheological hypothesis [14], spherical shell instability hypothesis [15], and solid–fluid coupling instability theory [16]. Wang et al. reported that coal and gas outbursts are the result of the comprehensive action of stress, the gas contained in the coal seam, and the physical and mechanical properties of the coal seam itself [17]. Field monitoring data, laboratory tests, and molecular dynamics simulation results confirmed that a large amount of gases such as CH_4 and CO burst out when the shear toughness zone of the coal seam was damaged [18–21]. Therefore, the construction of the atomic representation of coal–rock compound structure models and the adsorption characteristics and mechanical properties of methane in the model need further development.

Molecular dynamics simulation was first proposed by Alder and Wainwright in 1957 [22]. To date, molecular simulation technology has been successfully applied in the chemical [23], materials [24], and energy [25,26] industries. In 1942, the University of Pennsylvania built the first coal molecular structure model [27]. Hundreds of coal molecular structure models have since been successfully constructed worldwide. Recently, molecular dynamics simulation in coal and rock models has become an important tool for analysing the adsorption and desorption behaviour of CH_4, CO_2, and other gases in extreme environments [28–32]. In addition, Wang et al. used molecular dynamics to simulate the change in coal molecular structures and the type of gas generated under shear stress and pointed out that shear gas production is the main source of excessive gas emissions when coal and gas outburst disasters occur [20,21]. To explore the mineralization mechanism of coal-bearing graphite, Ma et al. constructed a high-rank coal molecular structure model of Fengxian in Shaanxi [33]. The CH_4 adsorption capacity of coal is influenced by different dynamic and static factors. The dynamic factors generated by the redistribution of the initial rock stress by coal mining or methane extraction, static factors such as coal ranks, moisture contents, temperatures, and minerals of methane adsorption in coal also have attracted extensive attention. Molecular dynamics simulation of coal or rock reflects the influence mechanism of temperature, pressure, water content, and other parameters on the molecular structures and the adsorbed gas therein through volume expansion, interaction energy, and radial distribution function. Zhang et al. constructed an anthracite molecular structure model of the Qinshui Basin and simulated the methane adsorption capacity under different adsorption pressure conditions and the changes in the mechanical properties of anthracite after saturated adsorption [30].

In this work, atomistic representations of a coal–rock compound structure of anthracite in the Qinshui Basin and coking coal in the Ordos Basin were constructed, and molecular dynamic simulations were performed to characterize methane adsorption and mechanical properties considering temperature, pressure, and mineral content. The response characteristics of different associated mineral types and contents to the adsorption characteristics and mechanical properties of methane in coal from the molecular level were explained, and a micro mechanism for the occurrence mechanism of rockburst and coal and gas outburst combined disasters was provided.

2. Molecular Structure Models

Combined with elemental analysis, Fourier transform infrared (FTIR) spectrometry, ^{13}C NMR spectroscopy, X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy of coal samples, the molecular structures of anthracite and coking coal samples, are constructed [34], so the detailed construction process has been overlapped. According to the test results, the 3D models of the molecular structure of the anthracite and coking coal are constructed in Materials Studio software 2020 (as shown in Figure 1). The chemical formulas of the anthracite and coking coal are $C_{220}H_{82}N_2O_{13}S_2$ and $C_{213}H_{114}O_{16}N_2S$, respectively, and the dimensions of their 3D models are 1.53 × 1.53 × 1.53 nm and 1.56 × 1.56 × 1.56 nm, respectively. The minerals on the coal surface are mainly kaolinite and calcite [35], thus, calcite and kaolinite molecular are added to the molecular structure models of the anthracite and coking coal to build the coal–rock compound molecular structure model with different mineral contents in Materials Studio software 2020 [36]. It is noted that the methane adsorption on the edges of kaolinite and calcite should be studied before the adsorption simulations in the compound models; the omission of this section is due to the methane isothermal adsorption on a single pure mineral surface (0 0 1) and coal surfaces having been presented and validated in our previous work [37].

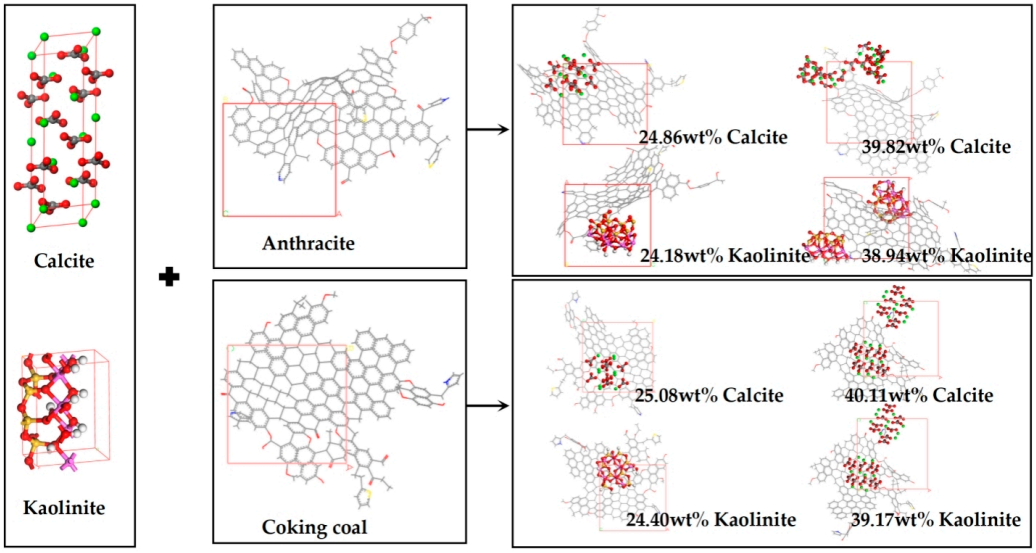


Figure 1. Schematic of coal–rock compound structure models.

In Figure 1, carbon, hydrogen, nitrogen, oxygen, sulphur, calcium, silicon, and aluminium atoms are represented by grey, white, blue, red, yellow, green, dark yellow, and magenta, respectively. Eight coal–rock compound molecular structure models with different kaolinite and calcite mineral contents were constructed. When adding calcite with mass fractions of 25.08w% and 40.11 wt% to the anthracite coal model, the chemical formulas of the model are $C_{230}H_{82}N_2O_{43}S_2Ca_{10}$ and $C_{240}H_{82}N_2O_{73}S_2Ca_{20}$, and the model sizes are 1.68 × 1.68 × 1.68 nm and 1.81 × 1.81 × 1.81 nm. When kaolinite with mass fractions of 24.18w% and 38.94 wt% is added to the anthracite coal model, the chemical formulas of the model are $C_{220}H_{90}N_2O_{45}S_2Al_8Si_8$ and $C_{220}H_{98}N_2O_{77}S_2Al_{16}Si_{16}$, with model sizes

of 1.68 × 1.68 × 1.68 nm and 1.80 × 1.80 × 1.80 nm. When adding calcite with mass fractions of 25.08w% and 40.11 wt% to the coking coal model, the chemical formulas of the model are $C_{230}H_{82}N_2O_{43}S_2Ca_{10}$ and $C_{240}H_{82}N_2O_{73}S_2Ca_{20}$, and the model sizes are 1.72 × 1.72 × 1.72 nm and 1.85 × 1.85 × 1.85 nm. When kaolinite with mass fractions of 24.40w% and 39.17 wt% is added to the coking coal model, the chemical formulas of the model are $C_{213}H_{122}O_{48}N_2SAl_8Si_8$ and $C_{213}H_{130}O_{80}N_2SAl_{16}Si_{16}$, with model sizes of 1.72 × 1.72 × 1.72 nm and 1.84 × 1.84 × 1.84 nm. Note that the size of the coal models created in the manuscript was indeed small (<2 nm), and readers should critically refer to refer to the simulation results.

3. Computational Methods

3.1. Simulation Scheme

As mentioned above, the minerals on the coal surface are mainly kaolinite and calcite; thus, calcite and kaolinite molecules were added to the molecular structure models of anthracite and coking coal to build the coal–rock compound molecular structure model with different mineral contents. The molecular dynamics simulation schemes include two coal molecular structure models and eight coal–rock compound models. For each coal molecular model, five adsorption temperatures (273.15, 283.15, 293.15, 303.15, and 313.15 K) and thirteen adsorption pressures (0.1, 0.3, 0.5, 1, 2, 3, 4, 5, ..., 10 MPa) were selected and calculated, Refs. [30,32], as showed in Table 1. Under each constant temperature, methane adsorption simulations with different adsorption pressures were carried out in each coal molecular model. Each coal–rock compound model was used to simulate different methane adsorption pressures at 273.15 K.

Table 1. Simulation Schemes.

Scheme	Molecular Models	Adsorption Pressure (MPa)	Adsorption Temperature (K)
1	Anthracite coal	0.1, 0.3, 0.5, 1, 2, 3...10	273.15, 283.15, 293.15, 303.15, 313.15
2	Anthracite + 24.86 wt% Calcite	0.1, 0.3, 0.5, 1, 2, 3...10	273.15
3	Anthracite + 39.82 wt% Calcite	0.1, 0.3, 0.5, 1, 2, 3...10	273.15
4	Anthracite + 24.18 wt% Kaolinite	0.1, 0.3, 0.5, 1, 2, 3...10	273.15
5	Anthracite + 38.94 wt% Kaolinite	0.1, 0.3, 0.5, 1, 2, 3...10	273.15
6	Coking coal	0.1, 0.3, 0.5, 1, 2, 3...10	273.15, 283.15, 293.15, 303.15, 313.15
7	Coking coal + 25.08 wt% Calcite	0.1, 0.3, 0.5, 1, 2, 3...10	273.15
8	Coking coal + 40.11 wt% Calcite	0.1, 0.3, 0.5, 1, 2, 3...10	273.15
9	Coking coal + 24.40 wt% Kaolinite	0.1, 0.3, 0.5, 1, 2, 3...10	273.15
10	Coking coal + 39.17 wt% Kaolinite	0.1, 0.3, 0.5, 1, 2, 3...10	273.15

3.2. Implementation of Molecular Simulations

The simulation details of molecular dynamics have been elaborated in detail in our previous work [30,37]. The force field utilized in the model construction and methane adsorption simulations was the Dreiding force field, and the simulations were completed by the Amorphous cell module, Sorption module, and Force module in the Materials Studio software 2020. The mechanical property simulation was completed in Mechanical Properties in the Force module, also using the Dreiding force field [38]. Note that a suitable force field selection is the key to the accuracy of molecular simulation results. The force field form selected in the simulation was only one of many force fields [38–45], and the simulation parameters and results were expected to be critically referenced by researchers. The cutoff distance for methane adsorption is 12.5 Å, and the amount of absolute adsorption was collected. To calculate the saturation sorption amount of methane, V_L, on modified coal, the Langmuir isothermal sorption equation was fitted to the test results.

$$V_{ab} = \frac{V_L P}{P_L + P} \quad (1)$$

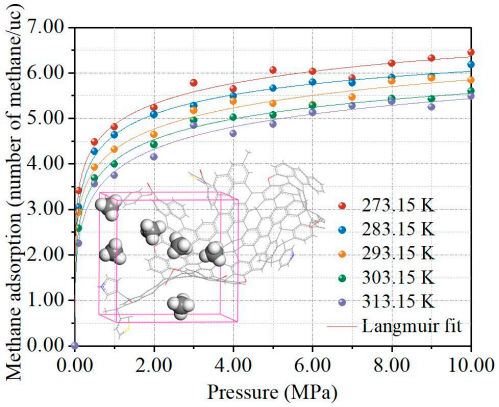
where P is the methane gas pressure, MPa; V_{ab} is the methane adsorption volume of coal at pressure P, mL/g; V_L is the methane saturation adsorption volume of coal at a certain temperature, mL/g, and P_L is the methane gas pressure at half of the saturation adsorption volume, MPa. The simulation results of mechanical properties were mainly presented in the form of a stiffness matrix, and then the mechanical parameters were obtained.

4. Results and Discussion

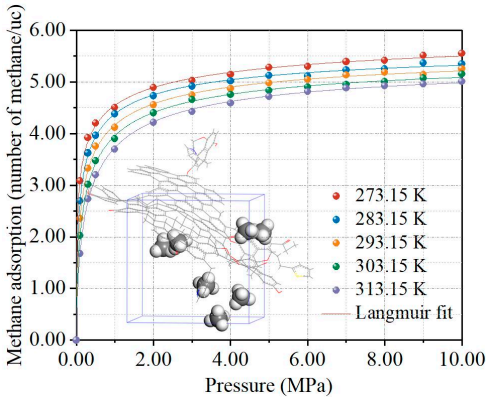
4.1. Methane Adsorption in Coal Models

To verify the correctness and applicability of the models and the applied force field, the adsorption of methane on the coal was fitted by the Langmuir equation. Figure 2 shows the methane isotherm adsorption curves and Langmuir fitting parameter, a, of the anthracite and coking coal at 273.15–313.15 K. When the adsorption temperature is constant, the adsorption capacity of methane molecules in the coal molecular structure model rapidly increases and then stabilises with increasing adsorption pressure, which is consistent with the Langmuir adsorption equation. When the adsorption pressure is constant, the amount of methane adsorption decreases with increasing temperature. In the molecular structure model of anthracite, the saturated adsorption amount of methane is 5.80 N/uc at 273.15 K; it decreases to 4.85 N/uc at 313.15 K. In the molecular structure model of coking coal, the methane adsorption amount is 5.23 N/uc at 273.15 K; it decreases to 4.78 N/uc at 313.15 K. Regarding the methane adsorption amount in the molecular structure model of coking coal under different temperature and pressure conditions, Zhu et al. built a coking coal model of the Chiyu coal mine and also found that the methane adsorption amount decreased with the increase in temperature [46]. A probe with a diameter equal to the methane molecular diameter (0.38 nm) was used to detect and count the micropores of the two coal molecular structure models. The results show that the free volumes of methane adsorbed by the anthracite and coking coal are 16.25×10^{-3} and 8.98×10^{-3} nm^3/uc, respectively, and that the accessible surface areas of methane are 0.45 and 0.56 nm^2/uc, respectively. The simulation results are consistent with Ref [47], and Cheng et al. reported that the micropores in coal are the main places where methane occurs, that is, the larger the micropore volume, the greater the methane adsorption capacity.

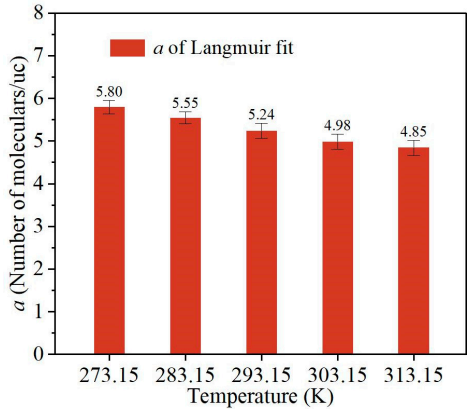
The adsorption heat of methane in coal is an important thermodynamic parameter for characterizing the adsorption behaviour of methane in coal; it serves as a quantitative indicator to evaluate the adsorption affinity of coal to methane [48]. The isothermal adsorption heat of methane in coal is generally calculated by the Clausius–Clapeyron equation [46,48]. Based on the methane adsorption as an exothermic process, Tang et al. used negative values to characterize the methane adsorption heat [48]. The simulation results show that the adsorption heat is expressed as a positive value. Figure 3 shows the isothermal adsorption heat simulation results of methane in the anthracite and coking coal at 273.15–313.15 K. The methane adsorption heat of anthracite is 28.13–28.57 Kj/mol, and that of coking coal is 26.23–26.48 Kj/mol. As the adsorption temperature increases from 273.15 K to 313.15 K, the methane adsorption heat of both coals shows an increasing trend, which is consistent with the results of Tang et al. and Zhang et al. [48,49].



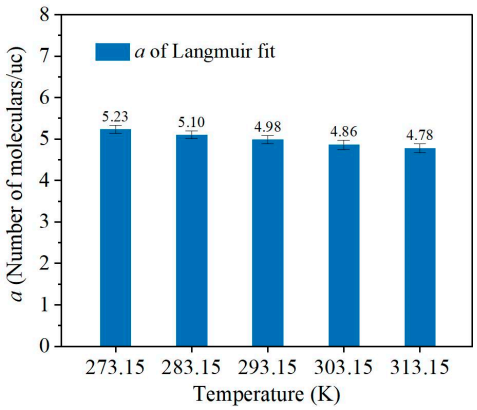
(**a**) Methane adsorption isotherm of anthracite.



(**b**) Methane adsorption isotherm of coking coal.

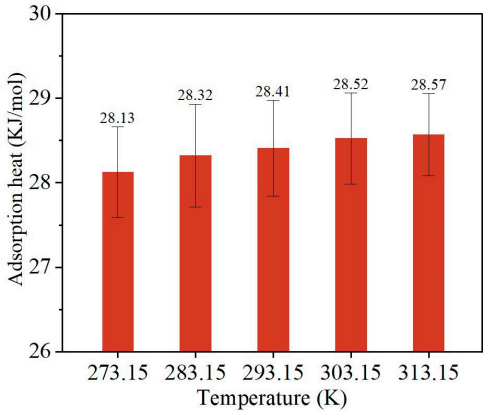


(**c**) Langmuir constant, a, of anthracite.

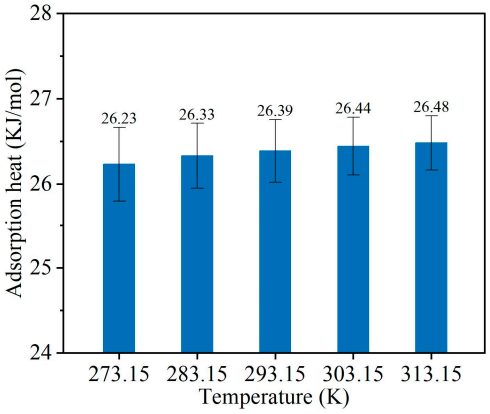


(**d**) Langmuir constant, a, of coking coal.

Figure 2. Methane adsorption isotherm of anthracite (**a**) and coking coal (**b**) at temperatures in the range of 273.15–313.15 k, and Langmuir fitting constant, a, of anthracite (**c**) and coking coal (**d**).



(**a**)



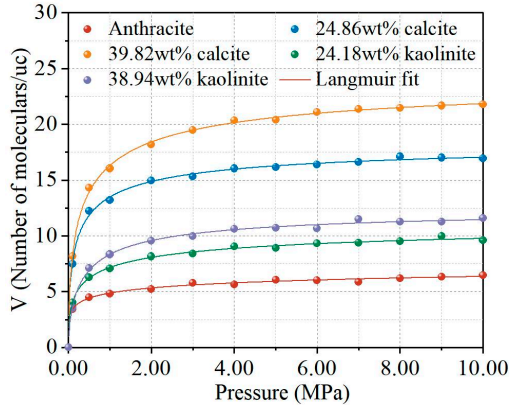
(**b**)

Figure 3. Adsorption heat of methane at different temperatures in anthracite and coking coal models. (**a**) Adsorption heat of methane in anthracite. (**b**) Adsorption heat of methane in coking coal.

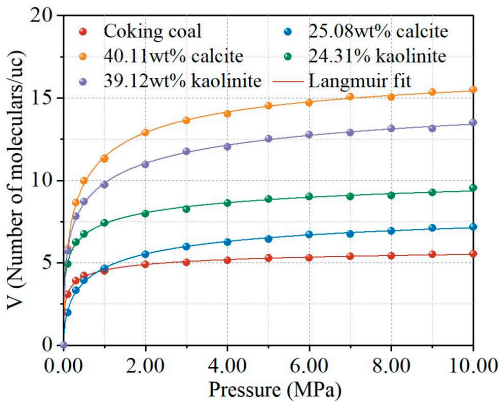
4.2. Effect of Minerals on Methane Adsorption of Coal-Rock Models

The adsorption of methane in the coal–rock compound model can also be fitted by the Langmuir equation [49]. To express the adsorption results clearly, a temperature of 273.15 K was selected to simulate the methane adsorption of compound coal–mineral models. Figure 4 shows the methane isotherm adsorption curves and Langmuir fitting parameter, a, in anthracite–rock and coking coal–rock compound models at 273 K. When the adsorption temperature is constant, the adsorption capacity of methane molecules in the coal–rock compound molecular structure model rapidly increases and then stabilizes with

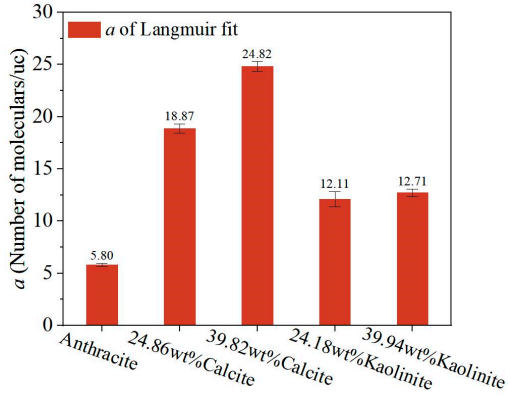
increasing adsorption pressure, which still conforms to the Langmuir adsorption model. When the adsorption pressure is constant, the methane adsorption capacity increases with increasing mineral content. In the anthracite–rock molecular structure model, the saturated adsorption capacity of methane reaches a maximum of 39.82 wt% calcite, which is 24.82 N/uc. In the coking coal–rock molecular structure model, the methane adsorption reaches a maximum of 40.11 wt% calcite, which is 15.18 N/uc. A probe with a diameter equal to the methane molecular diameter (0.38 nm) was selected to detect and count the micropores of the two coal–rock molecular structure models. In the molecular structure model of anthracite–rock, when the mineral content is 39.82 wt% calcite, the micropore volume reaches 0.70 nm^3/uc, which shows the large amount of methane adsorption when minerals are present. The results indicate that the highly developed micropores in clay minerals in coal are the main places for methane adsorption in coal, which is also reported by Feng et al. [50]. As can be seen in our previous paper [37,49] and the simulation results from Wang et al. [29], the surface of clay minerals like kaolinite also has the capacity to adsorb some methane. Besides, Feng et al. reported that, from the Scanning Electron Microscopy (SEM) micrographs of the same coal sample with different densities determined by the X-ray CT scan, the mesostructures of cell cavity pores with non-compact packing of the clay minerals appear to be the primary sites of methane adsorption in coal. Therefore, it is more generally accepted by researchers that the microporosity and surface structure parameters in clay minerals jointly affect the adsorption capacity.



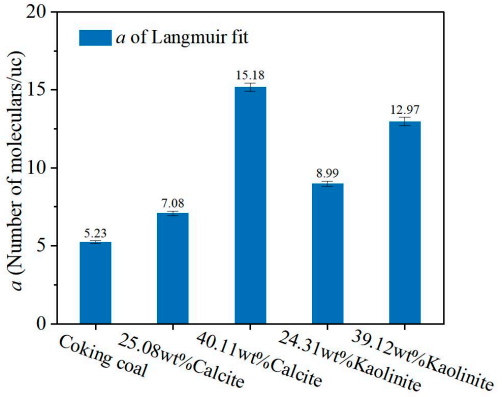
(**a**) Methane adsorption isotherm of anthracite–mineral model.



(**b**) Methane adsorption isotherm of coking coal–mineral model.



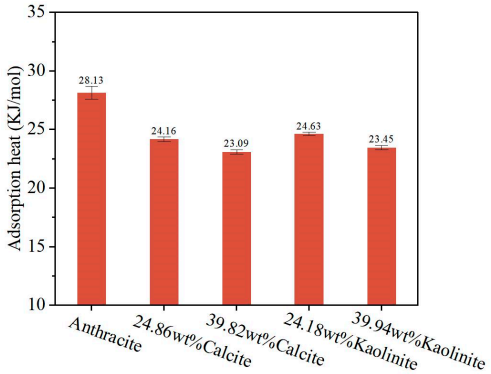
(**c**) Langmuir constant, a, of anthracite–mineral model.



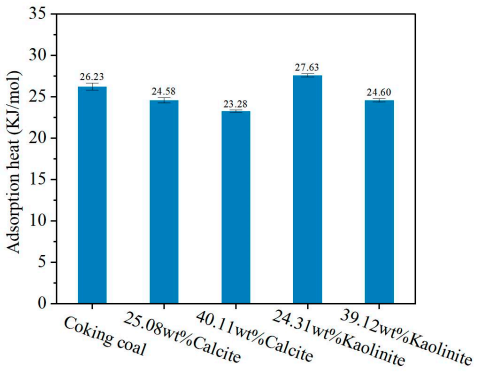
(**d**) Langmuir constant, a, of coking coal–mineral model.

Figure 4. Methane adsorption isotherm of the anthracite–mineral model (**a**) and coking coal–mineral model (**b**) at a temperature of 273.15 k, and Langmuir fitting constant, a, of the anthracite–mineral model (**c**) and coking coal–mineral model (**d**).

The isothermal adsorption heat of methane in the coal–rock compound model can also be calculated by the Clausius–Clapeyron equation [49,51]. Zhang et al. used the methane adsorption heat to characterize the energy release information of methane in kaolinite and determined that the reduction in the adsorption heat under the condition of high water content means that the interaction energy between methane molecules and kaolinite molecules was weakened [49]. Figure 5 shows the isothermal adsorption thermal simulation results of methane in the anthracite–rock model and coking coal–rock model at 273.15 K. When calcite and kaolinite minerals are added, the methane adsorption heat of anthracite is 28.13–23.09 Kj/mol, and that of coking coal is 26.23–23.28 Kj/mol. With an increase in the mineral content, the methane adsorption heat of the two coal rock compounds decreases, and the contribution of calcite is greater than that of kaolinite.



(**a**) Adsorption heat of methane in anthracite–mineral model.

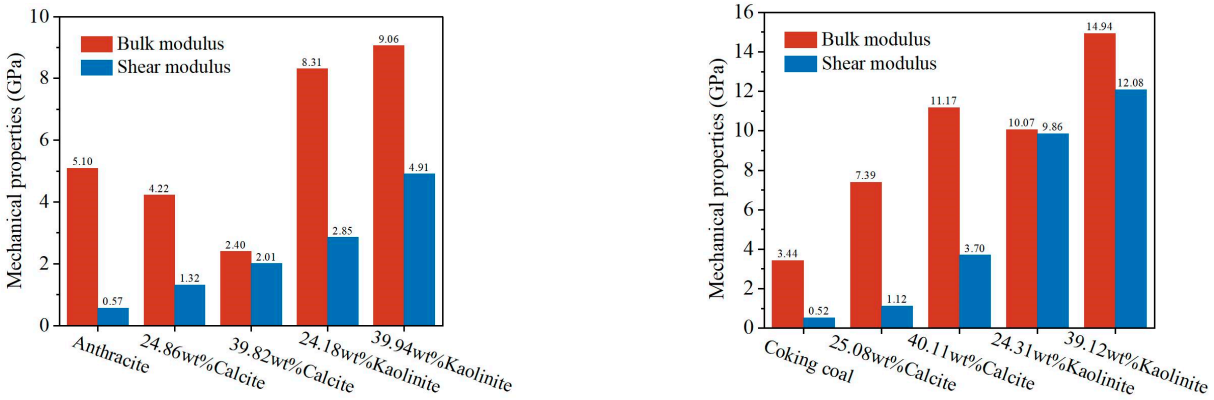


(**b**) Adsorption heat of methane in coking coal–mineral model.

Figure 5. Adsorption heat of methane at 273.15 K in anthracite–mineral model (**a**) and coking coal–mineral model (**b**).

4.3. Mechanical Properties of Coal-Rock Models

The bulk modulus and shear modulus in the coal–rock compound models were simulated in the Mechanical Properties of the Force module. Figure 6 shows the simulation results of the bulk modulus and shear modulus of the anthracite–rock model and coking coal–rock model under different calcite and kaolinite mineral contents. The bulk modulus of the anthracite–rock model decreases with the addition of calcite and tends to decrease with increasing calcite mineral content. The bulk modulus increases with the addition of the kaolinite mineral and tends to increase with increasing mineral content. The bulk modulus of the coking coal–rock model increases with the addition of calcite and kaolinite and tends to increase with increasing mineral content. Note that under the same mass percentage, the influence of kaolinite on the change in the bulk modulus and shear modulus of the two coal rock models is greater than that of calcite on the change in the two mechanical properties. The ratio of bulk modulus to shear modulus (E/G) is often used to estimate the brittle or ductile behaviour of materials. A high E/G represents plasticity, and a low E/G represents brittleness [52]. When minerals exist, the brittleness of the molecular model increases, and the brittleness index increases with increasing mineral content [53]. In addition, the atomic representation of coal–rock compound models is presented on a nanometre scale, which cannot illustrate the macroscopic mechanism of rockbursts and coal and gas outbursts. Larger coal–rock compound models will be constructed in our future work.



(**a**) Mechanical properties of anthracite–mineral model. (**b**) Mechanical properties of coking coal–mineral model.

Figure 6. Change in mechanical properties after the addition of calcite and kaolinite.

5. Conclusions

(1) The atomistic representations of the coking coal model and anthracite coal model considering the influence of minerals were constructed, which is an approach to characterize the methane adsorption and mechanical characteristics in coal.

(2) The amount of methane adsorption follows the order anthracite coal > coking coal, and the presence of minerals increases the methane adsorption capacity; the increased amount of methane adsorption follows the order calcite > kaolinite.

(3) The presence of calcite and kaolinite greatly increased the shear modulus of compound coal and mineral models. Notably, after the addition of calcite and kaolinite minerals, the brittleness of the model increases, and the brittleness index increases with increasing mineral content.

(4) Only calcite and kaolinite were considered typical co-associated minerals in coal, which is limited to explaining the methane adsorption and mechanical properties in all the coal–rock compound models. In addition, there are limited coal molecular structure models for molecular dynamic simulation work, and the construction of diversified coal molecular structure models is difficult but imperative. Thus, based on Graph Representation Learning and Graph Neural Networks, our team is committed to building diverse molecular structure models for almost all coal and rock, providing a theoretical basis for coal and rock dynamic disasters.

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