

## Article

# Molecular Simulation of Adsorption Separation of CO<sub>2</sub> from Combustion Exhaust Mixture of Commercial Zeolites

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**Abstract:** The adsorption thermodynamics and kinetics of CO<sub>2</sub> and six combustion products (H<sub>2</sub>O, SO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, NO and NO<sub>2</sub>) of two most commonly used commercial zeolites (13X and 5A) were studied based on validated molecular simulations. Adsorption isotherms at wide range of temperatures (253–333 K) were fitted by a Langmuir model, obtaining equilibrium parameters including the adsorption capacity, strength, heterogeneity and CO<sub>2</sub> selectivity from the mixture. The diffusion coefficients, isosteric adsorption heats and distributions of potential energy were simulated for further explanation. The comprehensive evaluation results suggest that, in actual combustion product mixtures, the presence of H<sub>2</sub>O in combustion products has a significant impact on CO<sub>2</sub> capture efficiency. Under the influence of water, the adsorption capacity of CO<sub>2</sub> was reduced by over 80%.

**Keywords:** CO<sub>2</sub> adsorption; adsorption thermodynamics; molecular simulation; carbon capture



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## 1. Introduction

CO<sub>2</sub> is the main component of fossil fuel combustion exhaust and a gas that is relevant to global warming [1]. Over the past decades, a number of technologies have been developed to prevent the release of CO<sub>2</sub> during combustion processes. Among them, the adsorption of CO<sub>2</sub> in nonporous materials is a proven suitable method that can reduce or eliminate CO<sub>2</sub> emissions, with the advantages of a small footprint, a low operating cost, a short startup process, etc. [2,3]. There are many different components in actual combustion products such as H<sub>2</sub>O, SO<sub>2</sub> and NO<sub>x</sub>. Aside from the toxicity itself, these gases also have strong interactions with sorbents, decreasing the CO<sub>2</sub> capture capacity of the sorbent over subsequent cycles [4–11]. Rege et al. [12] found that the presence of water could reduce the adsorption capacity in the adsorption process because of its strong adsorption force. Hu et al. [13,14] improved the structure of porous carbons, further enhancing the effectiveness of carbon capture. Therefore, in industrial practice, it is very important to select an adsorbent material to deal with complex components.

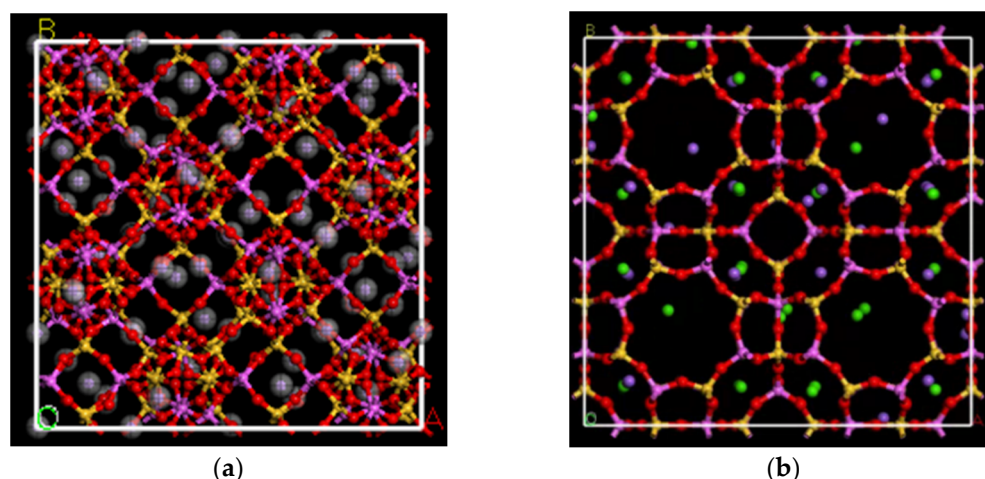
Among nano porous sorbents, zeolites are promising candidates for this application. Ordered zeolite structures have many desirable properties, such as high surface areas or thermal stability, that make them ideal materials for the storage, separation and purification of gas mixtures. Among all types of zeolites, 13X (FAU-type) and 5A (LTA-type) are the most widely used for CO<sub>2</sub> adsorption due to strong electrostatic fields generated in the skeleton, interacting strongly with CO<sub>2</sub> through quadrupole moments [15–17].

Adsorption thermodynamic properties, such as adsorption equilibrium, capacity, strength and selectivity within given operation conditions, are the most critical criteria for choosing adsorbents of CO<sub>2</sub> capture. For practical applications, the study of selectivity and adsorption thermodynamic properties in multicomponent systems is even more necessary. Previous experimental work has widely concentrated on the thermodynamics of CO<sub>2</sub> and other combustion products on zeolites under pure conditions. However, work conducted on CO<sub>2</sub>-containing mixtures with large temperature and pressure variations is rare because of high difficulty and a high cost. Molecular simulations are an effective method that can supplement experimental research [18–23]. They can enable people to explain experimental phenomena more intuitively from a microscopic perspective. In this paper, the adsorption properties of CO<sub>2</sub> and six combustion gas (O<sub>2</sub>, N<sub>2</sub>, NO, NO<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>O) for 13X and 5A zeolites at different temperatures (253–333 K) were obtained using grand canonical Monte Carlo (GCMC) and molecular dynamics (MD) simulations. Furthermore, adsorption selectivity was calculated to provide a theoretical discussion for CO<sub>2</sub> capture from combustion flue gas. In this study, CO<sub>2</sub> capture efficiency under complex gas composition conditions was comprehensively evaluated from both macro and micro perspectives, which will provide data support and a reference for the post combustion CO<sub>2</sub> capture process.

## 2. Computational Methods and Details

### 2.1. Models

The 13X and 5A skeleton models for molecular simulations were constructed by using Material Studio software (2019). Due to the unknown position of Al<sup>3+</sup> in the zeolite skeleton, a random allocation method was adopted, satisfying the Löwenstein rule. To ensure that the size of the three directions is greater than twice the radius of the segment, we constructed a  $2 \times 2 \times 2$  supercell. 13X zeolite has an FAU structure with a three-dimensional elliptical cross pore composed of four- and six-member rings. As shown in Figure 1a, we replaced the Al part in the FAU model with Si, introduced a Na<sup>+</sup> equilibrium charge and obtained a reasonable three-dimensional skeleton structure through geometric optimization. The symmetry of the structure is P1. The molecular formula of 13X is Na<sub>88</sub>Al<sub>88</sub>Si<sub>104</sub>O<sub>384</sub>, and the lattice length is 25.028 Å [20].



**Figure 1.** Zeolite models of (a) 13X and (b) 5A.

As shown in Figure 1b, 5A zeolite has an LTA-type structure. The ideal unit cell is equivalent to 8  $\alpha$ -cages and 24 cubic cages, and this structure belongs to the hexagonal system and the FM-3C space group. The molecular formula of 5A is Na<sub>32</sub>Ca<sub>32</sub>Al<sub>96</sub>Si<sub>96</sub>O<sub>384</sub>, and the lattice length is 24.55 Å [24].

## 2.2. Adsorbate–Adsorbent Interaction Potential

The Dreiding force field with the Lennard-Jones (L-J) potential function was adopted in the calculations. The interactive parameters,  $\varepsilon$  and  $\sigma$ , can be obtained according to the mixed calculation rule of Lorentz–Berthelot, as follows:

$$\begin{cases} \sigma_{ij} = (\sigma_i + \sigma_j) / 2 \\ \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \end{cases} \quad (1)$$

where  $\sigma_i$  and  $\sigma_j$  are the collision diameters (Å);  $\varepsilon_i$  and  $\varepsilon_j$  are the potential energy well depths (kcal/mol); and subscripts  $i$  and  $j$  refer to the types of atoms or molecules. Detailed data can be found in the Table S1.

## 2.3. Molecular Simulation Methods

### 2.3.1. GCMC Simulations

For the established unit cells of the zeolite models, GCMC simulations were used to calculate the adsorption equilibria and isosteric heat of adsorbates under periodic boundary conditions. In each run of the simulations, first, a zeolite framework was configured without adsorbents, and then the subsequent configuration was formed based on the Metropolis algorithm, which accepts or rejects the generation, disappearance, rotation and translation of adsorbents according to energy changes.

The distribution of all movements (exchange, conformation, rotation and translation) in each GCMC simulation was set to 20%, 20%, 40% and 20%, respectively. The Ewald summation method was used to handle electrostatic interactions, with an accuracy of  $10^{-5}$  kcal/mol. The atomic summation method was used to calculate the van der Waals interactions. The cutoff value of the Lennard-Jones interaction energy was determined to be 12.5 Å. The simulation length was  $1 \times 10^6$  steps.

The simulated environment is in a low-pressure state. Therefore, it can be considered that fugacity is equal to pressure, and the gas meets the state equation of an ideal gas. For the zeolite adsorption of small gas molecules, the adsorption isotherm generally conforms to the Langmuir model:

$$q = \frac{q_m K_p}{1 + K_p} \quad (2)$$

where  $q_m$  is the theoretical single molecule saturated adsorption capacity, mmol/g, and  $K$  is the Langmuir constant, L/mmol. The equilibrium selectivity,  $S$ , can be calculated as follows:

$$S_{1/2} = \frac{q_1 K_1}{q_2 K_2} \quad (3)$$

In a binary system, the selectivity can be calculated as follows:

$$S_{1/2} = \frac{q_1 p_2}{q_2 p_1} \quad (4)$$

where  $q$  is the saturated adsorption capacity of the gas, and  $p$  is the saturated adsorption pressures of the gas.

### 2.3.2. EMD Simulations

The molecular dynamics (MD) method is used to simulate the diffusion process of gas in zeolite in order to obtain the diffusion coefficient of the gas in the zeolite. Before MD simulations, it is necessary to load a gas molecule into the zeolite and obtain a low-energy configuration and to then optimize its structure. In MD simulations, the NVT ensemble is used, with an initial velocity set to random. The Nose hot bath method is used, with a time step of 1 fs and a total simulation time set to 200 ps, with the first 50 ps used for the

equilibrium structure and the last 150 ps used for the result calculations. The self-diffusion coefficient of a gas can be calculated from the Einstein equation:

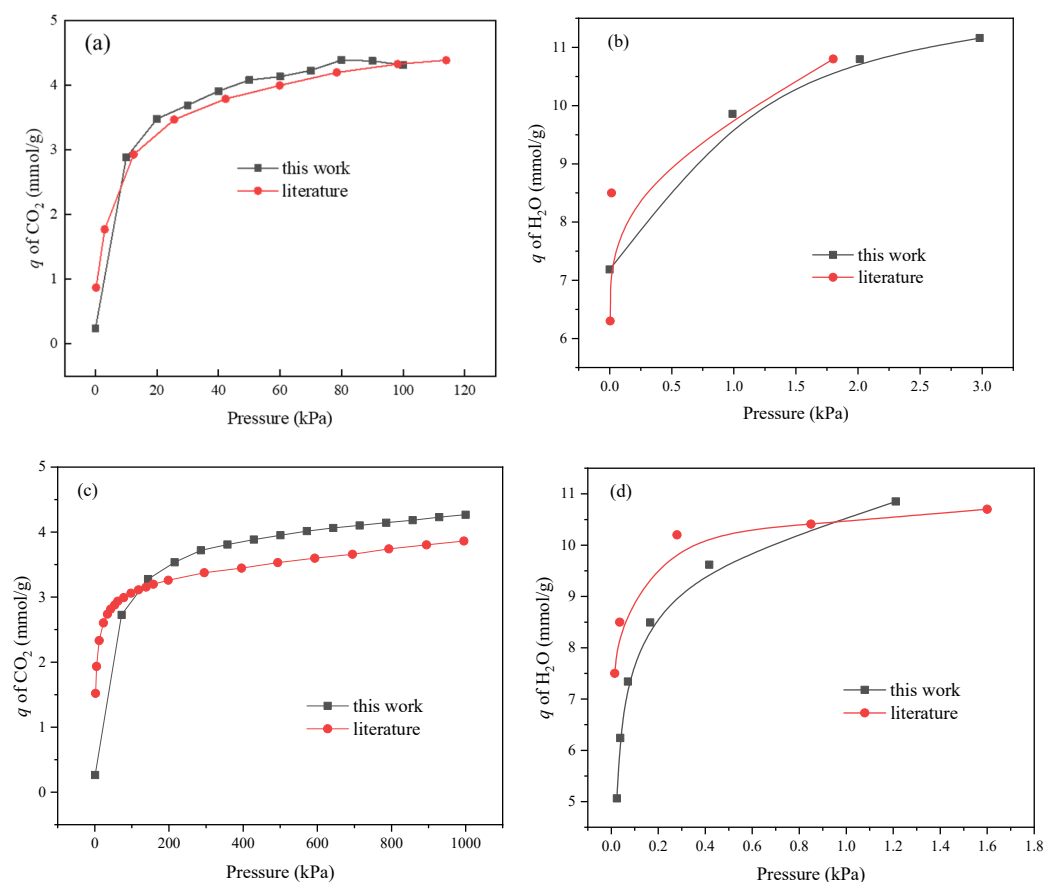
$$D_S = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle \quad (5)$$

where  $\langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle$  is the mean squared displacement (MSD) of gas molecules. When the slope of the log MSD–log t curves is 1, the simulation results converge. At this point, 1/6 of the slope of the MSD–t curve is the self-diffusion coefficient. When the gas concentration is quite low, the thermodynamic correction diffusion coefficient is approximately equal to the self-diffusion coefficient obtained from the simulation.

### 3. Results

#### 3.1. Validation of Model and Simulation

The adsorption isotherms of pure components were computed and compared to experimental data to validate the parameters of the force field. The calculated adsorption isotherms of 13X and 5A for CO<sub>2</sub> and H<sub>2</sub>O were compared with the literature values. As shown in Figure 2, the simulation results show good agreement with the experimental data, with a slight overestimation of the H<sub>2</sub>O adsorption capacity. The simulations were performed for rigid and clean zeolite structures, and experimental data were obtained from materials with structural defects or impurities that would lead to a lower adsorption capacity. The simulation method, zeolite models and force field parameters were well verified by the comparison results [10,25–27].



**Figure 2.** Comparison of isotherms between those of the literature and this article. CO<sub>2</sub> ((a), 0–100 kPa, 298 K) and H<sub>2</sub>O ((b), 0–3 kPa, 298 K) for 13X, and CO<sub>2</sub> ((c), 0–1000 kPa, 298 K) and H<sub>2</sub>O ((d), 0–1.6 kPa, 298 K) for 5A.

### 3.2. Adsorption Isotherms and Equilibrium Parameters of Pure Components

As shown in Figure 3, at 253–333 K, the pure component adsorption isotherms of CO<sub>2</sub>, H<sub>2</sub>O, SO<sub>2</sub>, NO, NO<sub>2</sub> and N<sub>2</sub> for 13X zeolite were calculated. In the combustion exhaust mixture, H<sub>2</sub>O mainly exists in a state of saturated vapor; therefore, the conditions of saturated vapor pressure at different temperatures were used for the H<sub>2</sub>O simulations in this study. The adsorption capacity, from high to low, is as follows: H<sub>2</sub>O > SO<sub>2</sub> > CO<sub>2</sub> > N<sub>2</sub> > NO > NO<sub>2</sub>. The adsorption capacity decreases with increases in temperature and increases with increases in pressure. H<sub>2</sub>O, CO<sub>2</sub> and SO<sub>2</sub> are more likely to reach saturation, because they carry more charges and have a stronger attraction to cations in zeolites. This is similar to the experimental data [28]. Table 1 shows the adsorption parameter values of the adsorption isotherm fitted by the Langmuir model, in which H<sub>2</sub>O and SO<sub>2</sub> more easily achieve saturated adsorption due to their good adsorption characteristics, whereas CO<sub>2</sub>, NO<sub>2</sub>, NO and N<sub>2</sub> have small adsorption capacities and slow adsorption processes. Even if the partial pressure of CO<sub>2</sub> is large, it is difficult to achieve saturated adsorption at high temperatures. This is because H<sub>2</sub>O and SO<sub>2</sub> carry more charges and have a stronger attraction to cations in zeolites.

Figure 4 shows the pure component adsorption isotherms for 5A zeolite. The adsorption parameters are shown in Table 2. The adsorption capacities of CO<sub>2</sub>, H<sub>2</sub>O and SO<sub>2</sub> gradually increase with increases in pressure under low-pressure conditions, and they gradually become stable and reach saturation with increases in pressure. However, O<sub>2</sub>, N<sub>2</sub>, NO and NO<sub>2</sub> do not reach saturation under the same pressure conditions. Under the same temperature conditions, the adsorption capacities of the seven gases are related as follows: H<sub>2</sub>O > SO<sub>2</sub> > CO<sub>2</sub> > O<sub>2</sub> > N<sub>2</sub> > NO > NO<sub>2</sub>. The adsorption capacity of each component decreases with increases in temperature, but the adsorption capacities of H<sub>2</sub>O and SO<sub>2</sub> are less affected by temperature.

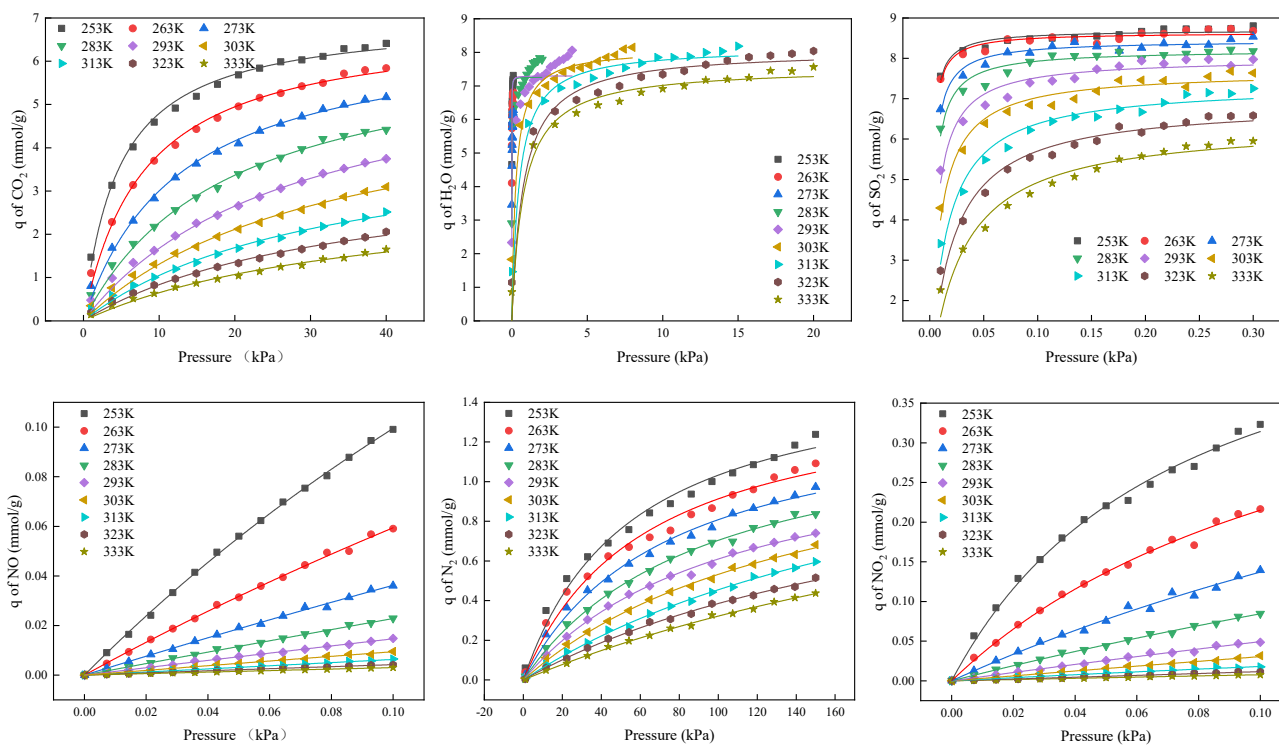


Figure 3. Adsorption isotherms (253–333 K) of 6 pure components for 13X.

Table 1. Adsorption parameters of pure components for 13X zeolite fitted by Langmuir model.

| Molecule         |                             | Temperature (K) |        |         |         |         |        |        |        |        |
|------------------|-----------------------------|-----------------|--------|---------|---------|---------|--------|--------|--------|--------|
|                  |                             | 253             | 263    | 273     | 283     | 293     | 303    | 313    | 323    | 333    |
| CO <sub>2</sub>  | $q$ (mmol·g <sup>−1</sup> ) | 7.02            | 6.91   | 6.76    | 6.56    | 6.36    | 5.49   | 4.38   | 3.63   | 3.07   |
|                  | $K$ (kPa <sup>−1</sup> )    | 0.215           | 0.126  | 0.080   | 0.053   | 0.036   | 0.031  | 0.031  | 0.030  | 0.027  |
|                  | $R^2$                       | 0.994           | 0.991  | 0.992   | 0.992   | 0.991   | 0.992  | 0.992  | 0.993  | 0.991  |
| H <sub>2</sub> O | $q$ (mmol·g <sup>−1</sup> ) | 15.28           | 14.10  | 13.12   | 13.31   | 13.11   | 13.33  | 13.35  | 12.95  | 12.13  |
|                  | $K$ (kPa <sup>−1</sup> )    | 1310.6          | 1344.7 | 1260.5  | 1076.4  | 1043.8  | 832.1  | 764.5  | 665.5  | 657.9  |
|                  | $R^2$                       | 0.636           | 0.670  | 0.655   | 0.709   | 0.700   | 0.747  | 0.731  | 0.738  | 0.762  |
| SO <sub>2</sub>  | $q$ (mmol·g <sup>−1</sup> ) | 8.70            | 8.64   | 8.44    | 8.21    | 8.00    | 7.68   | 7.36   | 6.91   | 6.40   |
|                  | $K$ (kPa <sup>−1</sup> )    | 607.70          | 597.84 | 365.094 | 286.103 | 159.413 | 108.38 | 65.080 | 47.440 | 33.317 |
|                  | $R^2$                       | 0.911           | 0.882  | 0.944   | 0.927   | 0.936   | 0.959  | 0.959  | 0.968  | 0.957  |
| O <sub>2</sub>   | $q$ (mmol·g <sup>−1</sup> ) | 0.69            | 0.73   | 0.78    | 1.19    | 0.73    | 0.37   | 0.76   | 0.55   | 0.45   |
|                  | $K$ (kPa <sup>−1</sup> )    | 0.128           | 0.076  | 0.044   | 0.019   | 0.024   | 0.038  | 0.012  | 0.013  | 0.012  |
|                  | $R^2$                       | 0.997           | 0.998  | 0.996   | 0.992   | 0.997   | 0.991  | 0.998  | 1.000  | 0.999  |
| NO               | $q$ (mmol·g <sup>−1</sup> ) | 0.57            | 0.54   | 0.52    | 0.48    | 0.51    | 0.43   | 0.40   | 0.74   | 0.110  |
|                  | $K$ (kPa <sup>−1</sup> )    | 77.457          | 41.615 | 20.934  | 11.777  | 5.768   | 3.963  | 2.439  | 0.759  | 0.163  |
|                  | $R^2$                       | 0.987           | 0.992  | 0.995   | 0.994   | 0.994   | 0.991  | 0.989  | 0.996  | 0.987  |
| N <sub>2</sub>   | $q$ (mmol·g <sup>−1</sup> ) | 1.60            | 1.48   | 1.41    | 1.36    | 1.26    | 1.34   | 1.52   | 1.28   | 1.47   |
|                  | $K$ (kPa <sup>−1</sup> )    | 0.018           | 0.016  | 0.014   | 0.011   | 0.009   | 0.007  | 0.004  | 0.004  | 0.003  |
|                  | $R^2$                       | 0.986           | 0.986  | 0.993   | 0.998   | 0.997   | 0.998  | 0.998  | 0.998  | 0.998  |
| NO <sub>2</sub>  | $q$ (mmol·g <sup>−1</sup> ) | 0.55            | 0.50   | 0.60    | 0.59    | 0.66    | 1.12   | 0.17   | 0.14   | 0.15   |
|                  | $K$ (kPa <sup>−1</sup> )    | 13.511          | 7.430  | 2.961   | 1.666   | 0.810   | 0.280  | 1.206  | 0.289  | 0.543  |
|                  | $R^2$                       | 0.995           | 0.995  | 0.992   | 0.997   | 0.993   | 0.997  | 0.990  | 0.992  | 0.995  |

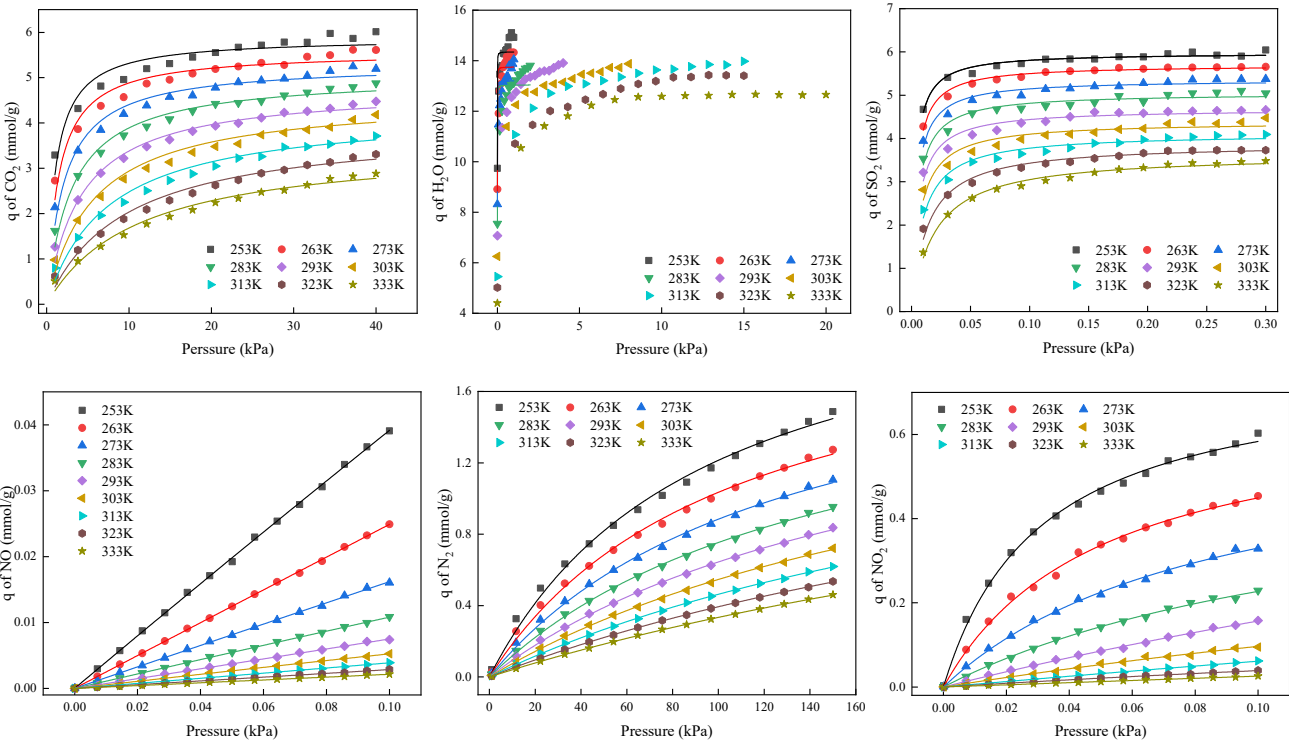


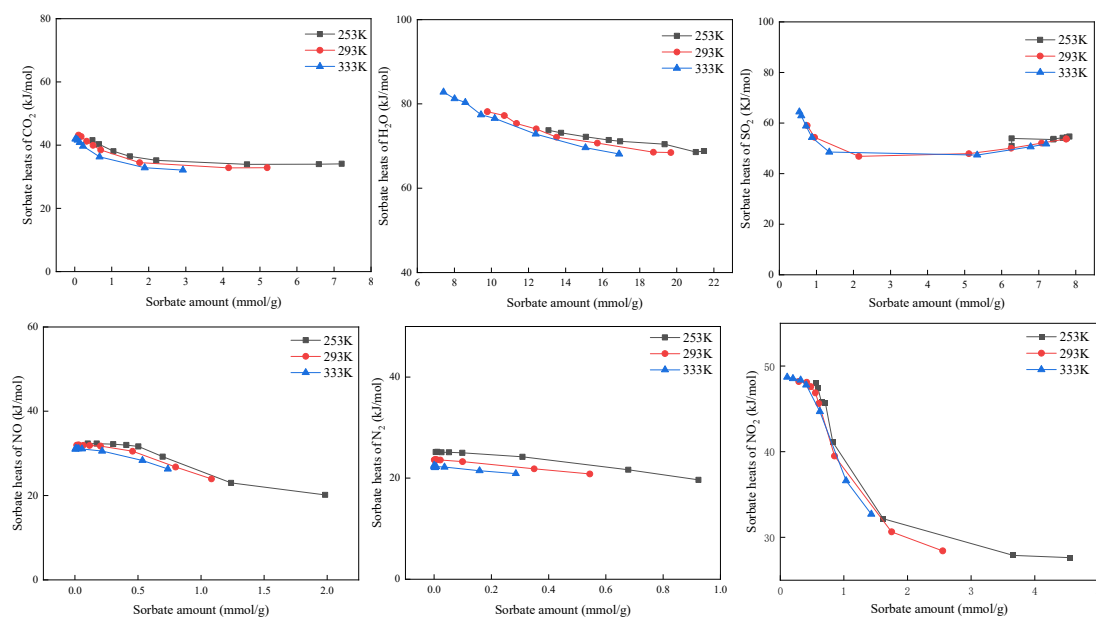
Figure 4. Adsorption isotherms (253–333 K) of 6 pure components for 5A.

**Table 2.** Adsorption parameters of pure components for 5A zeolite fitted by Langmuir model.

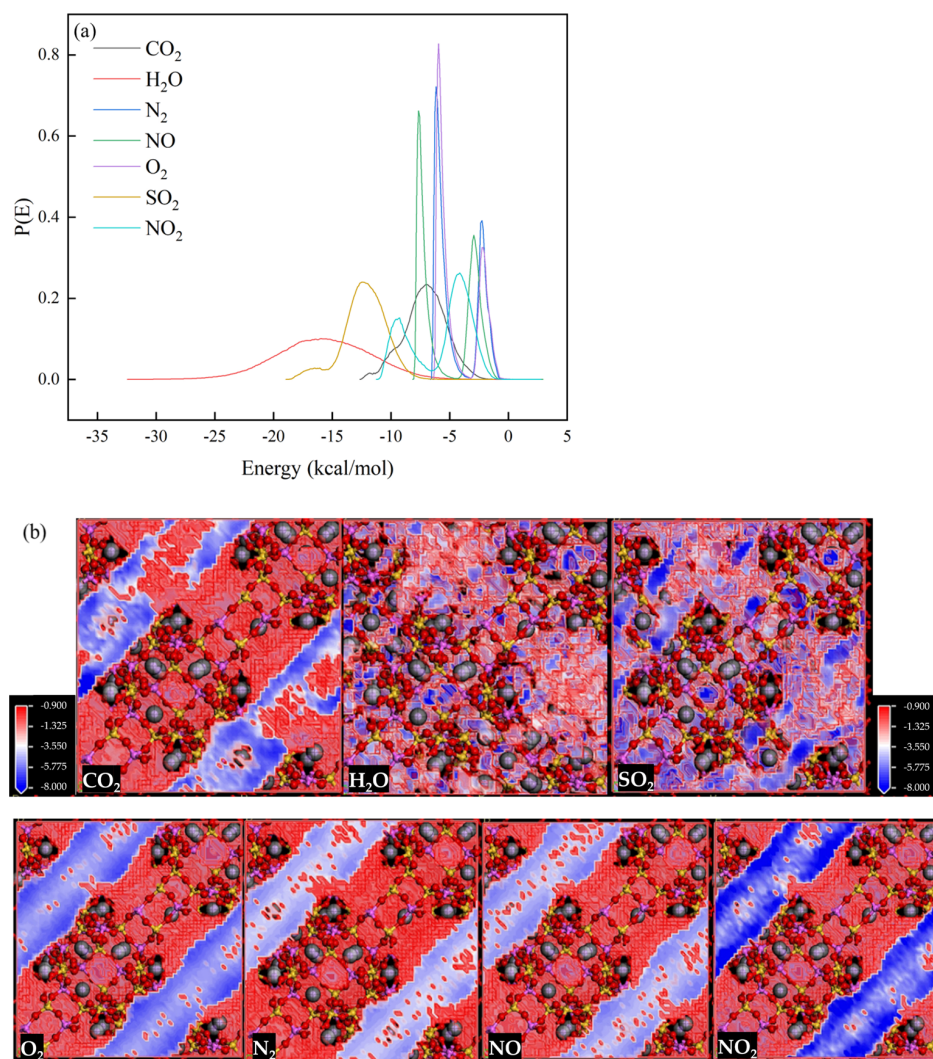
| Molecule         |                             | Temperature (K) |        |        |        |        |        |        |        |        |
|------------------|-----------------------------|-----------------|--------|--------|--------|--------|--------|--------|--------|--------|
|                  |                             | 253             | 263    | 273    | 283    | 293    | 303    | 313    | 323    | 333    |
| CO <sub>2</sub>  | $q$ (mmol·g <sup>−1</sup> ) | 5.88            | 5.57   | 5.31   | 5.06   | 4.79   | 4.57   | 4.29   | 3.95   | 3.55   |
|                  | $K$ (kPa <sup>−1</sup> )    | 0.94            | 0.70   | 0.49   | 0.33   | 0.24   | 0.18   | 0.13   | 0.10   | 0.09   |
|                  | $R^2$                       | 0.89            | 0.93   | 0.96   | 0.97   | 0.98   | 0.97   | 0.97   | 0.98   | 0.98   |
| H <sub>2</sub> O | $q$ (mmol·g <sup>−1</sup> ) | 14.35           | 13.75  | 13.21  | 13.04  | 13.15  | 13.12  | 13.15  | 12.69  | 12.29  |
|                  | $K$ (kPa <sup>−1</sup> )    | 2073.6          | 1798.1 | 1659.9 | 1353.9 | 1154.5 | 906.91 | 704.88 | 651.66 | 556.85 |
|                  | $R^2$                       | 0.87            | 0.87   | 0.86   | 0.89   | 0.91   | 0.97   | 0.96   | 0.86   | 0.91   |
| SO <sub>2</sub>  | $q$ (mmol·g <sup>−1</sup> ) | 7.76            | 7.68   | 7.50   | 7.36   | 7.26   | 7.23   | 7.01   | 6.89   | 6.82   |
|                  | $K$ (kPa <sup>−1</sup> )    | 590.77          | 570.10 | 529.12 | 523.12 | 505.01 | 487.54 | 412.57 | 411.66 | 387.27 |
|                  | $R^2$                       | 0.98            | 0.99   | 0.99   | 0.98   | 0.94   | 0.98   | 0.97   | 0.97   | 0.98   |
| O <sub>2</sub>   | $q$ (mmol·g <sup>−1</sup> ) | 1.73            | 1.54   | 1.47   | 1.36   | 1.25   | 1.20   | 1.15   | 1.07   | 1.05   |
|                  | $K$ (kPa <sup>−1</sup> )    | 0.030           | 0.019  | 0.016  | 0.009  | 0.008  | 0.0043 | 0.004  | 0.0038 | 0.0025 |
|                  | $R^2$                       | 0.99            | 0.99   | 0.99   | 0.99   | 0.99   | 0.99   | 0.99   | 0.99   | 0.99   |
| NO               | $q$ (mmol·g <sup>−1</sup> ) | 1.65            | 1.55   | 1.49   | 0.594  | 0.371  | 0.152  | 0.112  | 0.064  | 0.0360 |
|                  | $K$ (kPa <sup>−1</sup> )    | 0.35            | 0.24   | 0.23   | 0.18   | 0.18   | 0.15   | 0.12   | 0.10   | 0.09   |
|                  | $R^2$                       | 0.99            | 0.99   | 0.99   | 0.99   | 0.99   | 0.99   | 0.99   | 0.99   | 0.99   |
| N <sub>2</sub>   | $q$ (mmol·g <sup>−1</sup> ) | 2.35            | 2.13   | 2.02   | 1.88   | 1.88   | 1.85   | 1.79   | 1.80   | 1.81   |
|                  | $K$ (kPa <sup>−1</sup> )    | 0.01            | 0.0094 | 0.0077 | 0.0066 | 0.0052 | 0.0042 | 0.0035 | 0.0028 | 0.0022 |
|                  | $R^2$                       | 0.99            | 0.99   | 0.99   | 0.99   | 0.99   | 0.99   | 0.99   | 0.99   | 0.99   |
| NO <sub>2</sub>  | $q$ (mmol·g <sup>−1</sup> ) | 0.76            | 0.67   | 0.62   | 0.55   | 0.45   | 0.38   | 0.33   | 0.27   | 0.24   |
|                  | $K$ (kPa <sup>−1</sup> )    | 32.38           | 19.85  | 11.48  | 7.07   | 4.02   | 2.84   | 1.49   | 0.71   | 0.48   |
|                  | $R^2$                       | 0.99            | 0.99   | 0.99   | 0.99   | 0.99   | 0.99   | 0.99   | 0.99   | 0.99   |

As shown in Figure 5, the relationship between the adsorption heat of each gas and the adsorption capacity was calculated. In combination with the energy density distribution diagram shown in Figure 6a, the adsorption heat of each gas itself changes slightly with the adsorption capacity and decreases slightly with increases in the adsorption capacity (the absolute value increases). However, the size relationship for different gases is as follows: H<sub>2</sub>O < SO<sub>2</sub> < CO<sub>2</sub> < NO < NO<sub>2</sub> < N<sub>2</sub> < O<sub>2</sub>. The size of the adsorption heat reflects the adsorption strength of gas molecules for zeolite, which corresponds to the single-component adsorption mentioned above, and the adsorption strengths of H<sub>2</sub>O and SO<sub>2</sub> are higher. Figure 6b shows the adsorption configurations of various gases for 13X zeolite, visually displaying the adsorption sites of gas molecules on 13X zeolite. The red region has a smaller adsorption energy, the blue region has a larger adsorption energy, and H<sub>2</sub>O has the strongest adsorption energy.

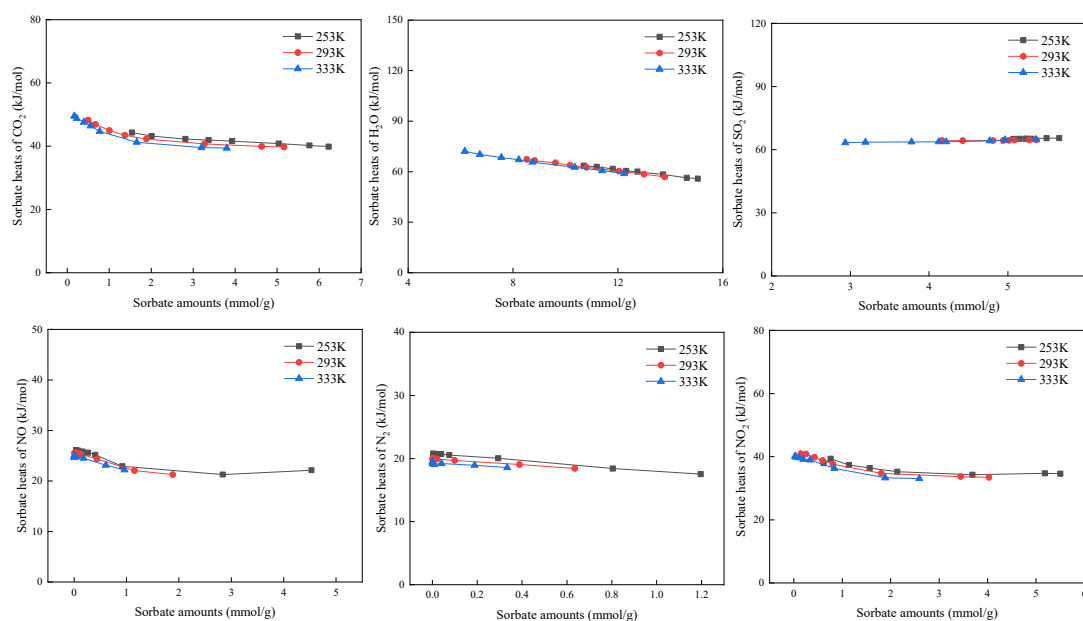
Figure 7 shows the relationship for the adsorption heat of each gas for 5A zeolite and the saturation adsorption amount, corresponding to the potential energy distribution curve and adsorption configuration, as shown in Figure 8. The adsorption heat of each gas slowly increases with increases in the saturated adsorption amount, but the overall change is not significant. The relationship for the adsorption heat of each gas is as follows: H<sub>2</sub>O < SO<sub>2</sub> < CO<sub>2</sub> < NO<sub>2</sub> < NO < N<sub>2</sub> < O<sub>2</sub>, corresponding to the adsorption strength of a pure component.



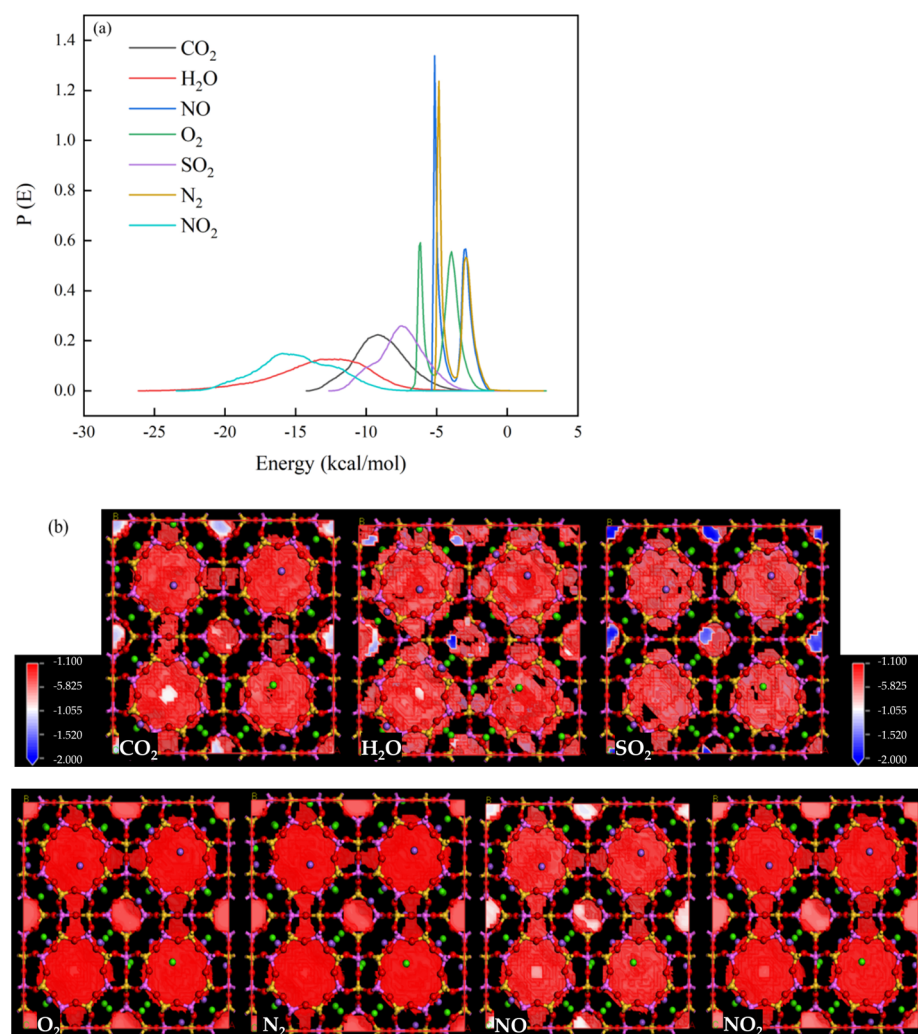
**Figure 5.** Variations in adsorption heat of pure components for 13X zeolite with adsorption capacity.



**Figure 6.** Simulated distributions (a) and profiles (b) of potential energy for 7 gases for 13X at 298 K, 100 kPa.



**Figure 7.** Variations in adsorption heat of pure components for 5A zeolite with adsorption capacity.



**Figure 8.** Simulated distributions (a) and profiles (b) of potential energy for 7 gases for 5A at 298 K, 100 kPa.

### 3.3. Adsorption Isotherms and Equilibrium Parameters in Mixture

The adsorption isotherms of each gas from the mixture are shown in Figures 9 and 10. The proportions of all gases in the mixture are 13.1% CO<sub>2</sub>, 0.1% SO<sub>2</sub>, 5.82% O<sub>2</sub>, 0.0158% NO and 0.00158% NO<sub>2</sub>. Based on the saturated vapor pressure of H<sub>2</sub>O at different temperatures, within the temperature range of 253–333 K, H<sub>2</sub>O accounts for 0.6082–10%, and the rest is supplemented by N<sub>2</sub>. For the adsorption capacity of 13X zeolite, it meets the following requirements: H<sub>2</sub>O > SO<sub>2</sub> > CO<sub>2</sub> > N<sub>2</sub> > O<sub>2</sub> > NO > NO<sub>2</sub>, which is consistent with the single-component rule. However, except for H<sub>2</sub>O molecules, the adsorption capacity of all other gases significantly decreases. The CO<sub>2</sub> adsorption capacity of 3.2 mmol/g in a single component decreases to 0.64 mmol/g, and the adsorption capacity decreases by 80%. The SO<sub>2</sub> adsorption capacity also decreases from 7.2 mmol/g to 0.3 mmol/g, with a decrease of 96%, whereas O<sub>2</sub>, NO, NO<sub>2</sub> and N<sub>2</sub> all decrease by an order of magnitude. This indicates that there is competitive adsorption when multi-component gases coexist, and H<sub>2</sub>O exhibits the best adsorption strength in a single component. Therefore, adsorption competition is the strongest in multi-component adsorption. Compared to single-component adsorption, the adsorption capacity of H<sub>2</sub>O hardly decreases. However, for 5A zeolite, due to the competitive adsorption between mixed components, H<sub>2</sub>O is extremely competitive, and the CO<sub>2</sub> adsorption capacity decreases. The SO<sub>2</sub> adsorption capacity decreases by 98%. The adsorption capacities of N<sub>2</sub> and NO are almost zero.

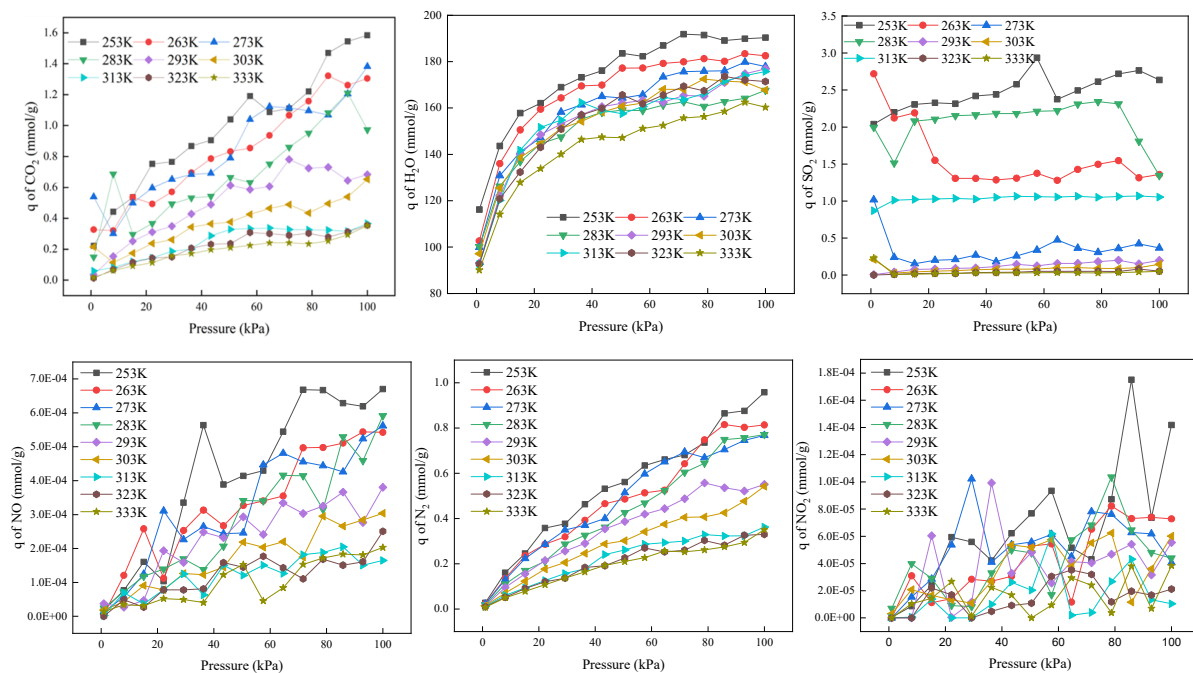


Figure 9. Adsorption isotherms (253–333 K) of mixture for 13X.

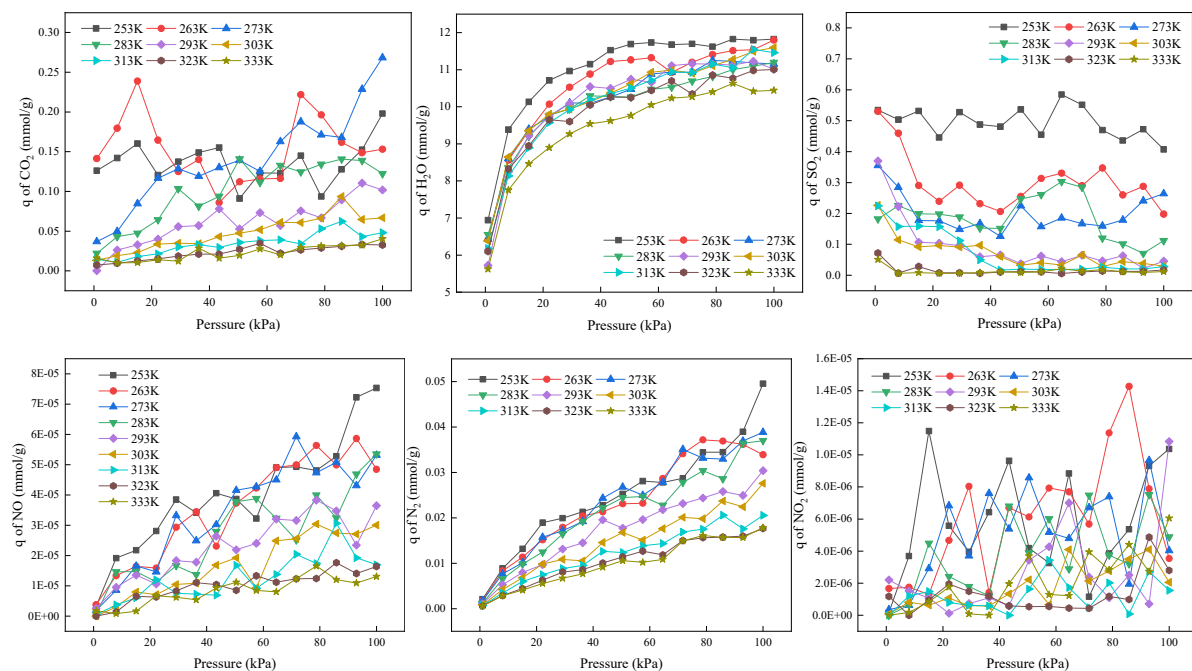


Figure 10. Adsorption isotherms (253–333 K) of mixture for 5A.

### 3.4. Self-Diffusion from Mixture

The diffusion coefficients calculated using the Einstein equation (Equation (4)) are shown in Tables 3 and 4, Figures S7 and S8. Their sizes meet the following rules:  $N_2 > NO > O_2 > SO_2 > CO_2 > NO_2$ , which is related to the gas molecular dynamics diameter and molecular polarity.  $N_2$ ,  $O_2$  and  $NO$  are diatomic small molecules, and their molecular dynamics diameter is smaller than the minimum pore size of 13X zeolites. Therefore, the diffusion coefficient is relatively large, and  $NO_2$ ,  $CO_2$  and  $SO_2$  are all triatomic molecule with larger dimensions than diatomic molecule. Due to the steric effects, their diffusion coefficients are relatively low. For the diffusion of  $H_2O$ , the MSD of  $H_2O$  is close to 0, and the diffusion coefficient is very small. This is due to the strong polarity of  $H_2O$  and the strong binding force of the pore on it, which prevents it from diffusing out of the pore.

Table 3. Diffusion coefficients of 7 gases for 13X zeolite at 253–333 K.

| Molecule         |                                           | Temperature (K) |      |      |      |      |      |      |      |       |
|------------------|-------------------------------------------|-----------------|------|------|------|------|------|------|------|-------|
|                  |                                           | 253             | 263  | 273  | 283  | 293  | 303  | 313  | 323  | 333   |
| CO <sub>2</sub>  | Ds ( $\times 10^{-10}$ m <sup>2</sup> /s) | 1.25            | 1.18 | 0.91 | 1.50 | 2.61 | 3.27 | 2.38 | 1.01 | 2.13  |
|                  | R <sup>2</sup>                            | 0.98            | 0.95 | 0.99 | 0.99 | 0.99 | 0.96 | 0.99 | 0.99 | 0.99  |
| H <sub>2</sub> O | Ds ( $\times 10^{-10}$ m <sup>2</sup> /s) | -               | -    | -    | -    | -    | -    | -    | -    | -     |
|                  | R <sup>2</sup>                            | -               | -    | -    | -    | -    | -    | -    | -    | -     |
| SO <sub>2</sub>  | Ds ( $\times 10^{-10}$ m <sup>2</sup> /s) | 1.37            | 1.16 | 0.88 | 1.23 | 0.85 | 1.74 | 1.35 | 5.69 | 1.38  |
|                  | R <sup>2</sup>                            | 0.99            | 0.99 | 0.98 | 0.98 | 0.99 | 0.97 | 0.99 | 0.98 | 0.99  |
| O <sub>2</sub>   | Ds ( $\times 10^{-10}$ m <sup>2</sup> /s) | 2.41            | 5.34 | 2.17 | 4.00 | 2.32 | 4.80 | 2.48 | 4.24 | 2.46  |
|                  | R <sup>2</sup>                            | 0.99            | 0.97 | 0.97 | 0.99 | 0.99 | 0.99 | 0.98 | 0.99 | 0.97  |
| NO               | Ds ( $\times 10^{-10}$ m <sup>2</sup> /s) | 2.85            | 7.33 | 4.16 | 2.08 | 1.25 | 6.77 | 2.60 | 2.60 | 5.11  |
|                  | R <sup>2</sup>                            | 0.98            | 0.99 | 0.97 | 0.91 | 0.93 | 0.98 | 0.99 | 0.99 | 0.98  |
| N <sub>2</sub>   | Ds ( $\times 10^{-10}$ m <sup>2</sup> /s) | 6.25            | 5.23 | 3.04 | 4.37 | 2.49 | 4.25 | 7.07 | 3.53 | 10.07 |
|                  | R <sup>2</sup>                            | 0.99            | 0.99 | 0.94 | 0.99 | 0.89 | 0.98 | 0.99 | 0.97 | 0.99  |
| NO <sub>2</sub>  | Ds ( $\times 10^{-10}$ m <sup>2</sup> /s) | 0.71            | 0.62 | 0.45 | 0.33 | 0.62 | 0.74 | 1.07 | 1.26 | 0.68  |
|                  | R <sup>2</sup>                            | 0.99            | 0.97 | 0.99 | 0.99 | 0.98 | 0.99 | 0.98 | 0.98 | 0.98  |

**Table 4.** Diffusion coefficients of 7 gases for 5A zeolite at 253–333 K.

| Molecule         |                                           | Temperature (K) |       |       |       |       |       |       |        |        |
|------------------|-------------------------------------------|-----------------|-------|-------|-------|-------|-------|-------|--------|--------|
|                  |                                           | 253             | 263   | 273   | 283   | 293   | 303   | 313   | 323    | 333    |
| CO <sub>2</sub>  | Ds ( $\times 10^{-10}$ m <sup>2</sup> /s) | 2.79            | 3.48  | 5.83  | 8.18  | 9.88  | 13.16 | 17.57 | 23.55  | 31.02  |
|                  | R <sup>2</sup>                            | 0.96            | 0.98  | 0.99  | 0.99  | 0.99  | 0.96  | 0.99  | 0.99   | 0.99   |
| H <sub>2</sub> O | Ds ( $\times 10^{-10}$ m <sup>2</sup> /s) | -               | -     | -     | -     | -     | -     | -     | -      | -      |
|                  | R <sup>2</sup>                            | -               | -     | -     | -     | -     | -     | -     | -      | -      |
| SO <sub>2</sub>  | Ds ( $\times 10^{-10}$ m <sup>2</sup> /s) | -               | -     | -     | -     | -     | -     | -     | -      | -      |
|                  | R <sup>2</sup>                            | -               | -     | -     | -     | -     | -     | -     | -      | -      |
| O <sub>2</sub>   | Ds ( $\times 10^{-10}$ m <sup>2</sup> /s) | 16.30           | 25.10 | 37.53 | 46.42 | 62.83 | 70.38 | 84.43 | 113.82 | 141.02 |
|                  | R <sup>2</sup>                            | 0.98            | 0.98  | 0.99  | 0.98  | 0.99  | 0.99  | 0.99  | 0.99   | 0.97   |
| NO               | Ds ( $\times 10^{-10}$ m <sup>2</sup> /s) | 13.58           | 15.10 | 15.69 | 20.08 | 23.68 | 27.32 | 28.82 | 32.42  | 36.15  |
|                  | R <sup>2</sup>                            | 0.98            | 0.99  | 0.98  | 0.99  | 0.99  | 0.99  | 0.99  | 0.99   | 0.99   |
| N <sub>2</sub>   | Ds ( $\times 10^{-10}$ m <sup>2</sup> /s) | 8.49            | 9.87  | 12.63 | 15.26 | 18.90 | 23.85 | 28.08 | 32.50  | 36.02  |
|                  | R <sup>2</sup>                            | 0.98            | 0.99  | 0.98  | 0.98  | 0.99  | 0.99  | 0.99  | 0.99   | 0.99   |
| NO <sub>2</sub>  | Ds ( $\times 10^{-10}$ m <sup>2</sup> /s) | 8.49            | 9.87  | 12.63 | 15.26 | 18.90 | 23.85 | 28.08 | 32.50  | 36.02  |
|                  | R <sup>2</sup>                            | 0.98            | 0.99  | 0.98  | 0.98  | 0.99  | 0.99  | 0.99  | 0.99   | 0.99   |

For the MSD values of each gas for 5A zeolite, the relationship is O<sub>2</sub> > NO > N<sub>2</sub> > CO<sub>2</sub> > NO<sub>2</sub>, where SO<sub>2</sub> and H<sub>2</sub>O fail to diffuse. The pore size of 5A zeolite is smaller than that of 13X, which has a stronger binding force on gas molecules, making it difficult for SO<sub>2</sub> and H<sub>2</sub>O to diffuse.

### 3.5. Adsorption Selectivity

As shown in Tables 5 and 6, the equilibrium selectivity of CO<sub>2</sub> and other pure components for 13X is calculated using Formula (3). The equilibrium selectivity of CO<sub>2</sub> during competitive adsorption with other components in the mixture is calculated using Formula (4). The simulation process is as follows: Under one atmospheric pressure, CO<sub>2</sub> is 13.1%, and the proportions of the other gas components are as follows: 0.1% SO<sub>2</sub>, 5.82% O<sub>2</sub>, 0.0158% NO and 0.00158% NO<sub>2</sub>. H<sub>2</sub>O is based on its saturated vapor pressure at different temperatures, and the rest is supplemented by N<sub>2</sub>.

**Table 5.** Adsorption selectivity for 13X zeolite at 253–333 K.

|         |                                   | Temperature (K) |        |        |        |        |        |        |        |        |
|---------|-----------------------------------|-----------------|--------|--------|--------|--------|--------|--------|--------|--------|
|         | S                                 | 253             | 263    | 273    | 283    | 293    | 303    | 313    | 323    | 333    |
| Pure    | CO <sub>2</sub> /SO <sub>2</sub>  | 3506.1          | 5931.2 | 5708.1 | 6799.2 | 5608.6 | 4845.2 | 3475.7 | 3021.8 | 2590.7 |
|         | CO <sub>2</sub> /H <sub>2</sub> O | 13,281          | 21,772 | 30,636 | 41,471 | 60,181 | 64,566 | 74,059 | 79,445 | 96,961 |
|         | CO <sub>2</sub> /O <sub>2</sub>   | 17.2            | 15.7   | 15.7   | 15.6   | 13.1   | 12.3   | 15.2   | 15.2   | 15.0   |
|         | CO <sub>2</sub> /N <sub>2</sub>   | 51.9            | 36.7   | 28.4   | 23.7   | 19.3   | 19.5   | 21.2   | 19.7   | 19.9   |
|         | CO <sub>2</sub> /NO               | 29.3            | 25.8   | 20.2   | 16.4   | 12.9   | 9.9    | 7.1    | 5.2    | 4.3    |
|         | CO <sub>2</sub> /NO <sub>2</sub>  | 4.9             | 4.3    | 3.3    | 2.8    | 2.4    | 1.8    | 1.5    | 0.4    | 1.0    |
| Mixture | CO <sub>2</sub> /SO <sub>2</sub>  | 112.1           | 106.8  | 80.7   | 65.0   | 76.4   | 70.8   | 116.9  | 140.0  | 144.9  |
|         | CO <sub>2</sub> /H <sub>2</sub> O | 3403.9          | 3595.9 | 3282.0 | 2190.3 | 1828.9 | 865.9  | 964.0  | 622.0  | 608.7  |
|         | CO <sub>2</sub> /O <sub>2</sub>   | 7.8             | 0.0    | 4.0    | 0.1    | 2.5    | 0.1    | 46.9   | 38.8   | 31.5   |
|         | CO <sub>2</sub> /N <sub>2</sub>   | 108.1           | 98.7   | 78.3   | 55.2   | 45.8   | 42.4   | 31.8   | 28.7   | 23.5   |
|         | CO <sub>2</sub> /NO               | 14.7            | 16.5   | 16.7   | 10.2   | 7.5    | 7.5    | 5.6    | 6.4    | 4.9    |
|         | CO <sub>2</sub> /NO <sub>2</sub>  | 9.2             | 1.4    | 10.0   | 4.7    | 2.5    | 3.0    | 3.3    | 2.6    | 3.0    |

**Table 6.** Adsorption selectivity for 5A zeolite at 253–333 K.

|         |                                   | Temperature (K) |        |        |        |        |        |        |        |        |
|---------|-----------------------------------|-----------------|--------|--------|--------|--------|--------|--------|--------|--------|
|         | S                                 | 253             | 263    | 273    | 283    | 293    | 303    | 313    | 323    | 333    |
| Pure    | CO <sub>2</sub> /SO <sub>2</sub>  | 360             | 403.9  | 506.2  | 613.5  | 739    | 757.7  | 777.4  | 699.5  | 586.9  |
|         | CO <sub>2</sub> /H <sub>2</sub> O | 5365            | 6297   | 8456   | 10,501 | 13,187 | 14,491 | 15,818 | 19,745 | 21,400 |
|         | CO <sub>2</sub> /O <sub>2</sub>   | 96.8            | 128.1  | 106    | 131    | 107.1  | 157.5  | 126.8  | 102.7  | 121.1  |
|         | CO <sub>2</sub> /N <sub>2</sub>   | 220.9           | 195.2  | 165    | 134    | 117.5  | 105.9  | 93.8   | 83.2   | 78.1   |
|         | CO <sub>2</sub> /NO               | 9.4             | 10.5   | 7.3    | 15.3   | 17.2   | 34.6   | 40.2   | 59     | 96.1   |
|         | CO <sub>2</sub> /NO <sub>2</sub>  | 0.2             | 0.3    | 0.4    | 0.4    | 0.6    | 0.7    | 1.2    | 2.2    | 2.7    |
| Mixture | CO <sub>2</sub> /SO <sub>2</sub>  | 593.1           | 558.4  | 534.2  | 542.3  | 480.5  | 549.8  | 494.5  | 483.0  | 376.3  |
|         | CO <sub>2</sub> /H <sub>2</sub> O | 1396.9          | 1337.4 | 1418.8 | 966.2  | 619.6  | 506.5  | 399    | 416.1  | 480.1  |
|         | CO <sub>2</sub> /O <sub>2</sub>   | 266.6           | 238.7  | 234.3  | 200.4  | 180.5  | 162.5  | 140.2  | 122.2  | 108.4  |
|         | CO <sub>2</sub> /N <sub>2</sub>   | 375.3           | 318.1  | 256.1  | 231.7  | 189.4  | 166.1  | 140.2  | 122.3  | 105.5  |
|         | CO <sub>2</sub> /NO               | 25.6            | 31.7   | 27.3   | 32.2   | 32.3   | 33.5   | 28.8   | 26.1   | 21.5   |
|         | CO <sub>2</sub> /NO <sub>2</sub>  | 4.7             | 4.5    | 3.3    | 3.1    | 3.4    | 3.9    | 4.2    | 3.5    | 3.8    |

#### 4. Conclusions

Adsorption isotherms and the self-diffusion of CO<sub>2</sub> and six combustion gases for 13X and 5A zeolites were obtained using molecular simulations based on highly validated gas–zeolite interaction models. Furthermore, the adsorption selectivity of CO<sub>2</sub> and other gases was discussed. The research results indicate that, for the pure component of the seven gases for the 13X and 5A zeolites, the Langmuir model shows good agreement with the isotherms and gives equilibrium parameters and thermodynamic constants for each adsorbate–adsorbent pair. Under the same temperature conditions, the relationship for the adsorption capacities of the seven gases is as follows: H<sub>2</sub>O > SO<sub>2</sub> > CO<sub>2</sub> > N<sub>2</sub> > O<sub>2</sub> > NO > NO<sub>2</sub>. For the mixture, H<sub>2</sub>O competes with CO<sub>2</sub> for adsorption sites, resulting in a significant decrease in the adsorption capacities of 13X and 5A for CO<sub>2</sub>. Compared to the pure component, the adsorption capacity of H<sub>2</sub>O remains almost unchanged, with the CO<sub>2</sub> adsorption reduced by 80% (13X) and 83% (5A), respectively. The diffusion coefficients of the seven gas molecules are as follows: N<sub>2</sub> > NO > O<sub>2</sub> > SO<sub>2</sub> > CO<sub>2</sub> > NO<sub>2</sub> (for 13X) and O<sub>2</sub> > NO > N<sub>2</sub> > CO<sub>2</sub> > NO<sub>2</sub> (for 5A). This is related to the dynamic diameters of gas molecules and the polarity of molecules. The binding force of pores on H<sub>2</sub>O is strong, causing it to not diffuse out of the pores. The pore size of 5A is smaller than that of 13X, making it difficult for SO<sub>2</sub> to diffuse into 5A.

**Supplementary Materials:** The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/pr11102987/s1>: Table S1: L-J potential function parameters; Figure S1: Isotherms of pure components for 13X; Figure S2: Isotherms of pure components for 5A; Figure S3: Variations in adsorption heat of pure components for 13X zeolite with adsorption capacity; Figure S4: Variations in adsorption heat of pure components for 5A zeolite with adsorption capacity; Figure S5: Isotherms of mixture for 13X; Figure S6: Isotherms of mixture for 5A; Figure S7: Variations in diffusion coefficients with temperature for (a) CO<sub>2</sub>, (b) H<sub>2</sub>O, (c) SO<sub>2</sub>, (d) O<sub>2</sub>, (e) N<sub>2</sub>, (f) NO and (g) NO<sub>2</sub> for 13X; Figure S8: Variations in diffusion coefficients with temperature for (a) CO<sub>2</sub>, (b) H<sub>2</sub>O, (c) SO<sub>2</sub>, (d) O<sub>2</sub>, (e) N<sub>2</sub>, (f) NO and (g) NO<sub>2</sub> for 5A; Figure S9: Adsorption kinetics selectivity of (a) SO<sub>2</sub>, (b) O<sub>2</sub>, (c) N<sub>2</sub>, (d) NO and (e) NO<sub>2</sub> from CO<sub>2</sub> for 13X; Figure S10: Adsorption kinetics selectivity of (a) O<sub>2</sub>, (b) N<sub>2</sub>, (c) NO and (d) NO<sub>2</sub> from CO<sub>2</sub> for 5A.

**Author Contributions:** Conceptualization, Y.W., S.W. and Z.L.; methodology, X.J.; software, X.Q.; validation, L.L.; investigation, X.Y.; data curation, S.G.; writing—original draft preparation, C.Z. All authors have read and agreed to the published version of the manuscript.

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