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Adsorption behaviors of CO_2 and CH_4 on zeolites JSR and Na_nJSR using the GCMC simulations

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Abstract The adsorption behaviors of CO_2 and CH_4 on new siliceous zeolites JSR and Na_nJSR ($n = 2, 8, 16$) were simulated using the Grand Canonical Monte Carlo method. The adsorption isotherms of CO_2 became higher with an increase in the Na^+ number at a low pressure range (<150 kPa), whereas the isotherms showed a crossover with increasing pressure and the adsorption amount became smaller at a high pressure range (>850 kPa). With an increase in Na^+ number, the pore volume decreased as the pore space was occupied by increasing Na^+ ions. Additionally, two energy peaks on the interaction energy curves implied that CO_2 was adsorbed on two active sites. On the other hand, the adsorption amount of CH_4 decreased with an increase in the Na^+ number and only one energy peak was observed. Adsorption isotherms were well fitted with the Langmuir and Freundlich equations up to 1000 kPa and the adsorption affinity of CO_2 on Na_{16}JSR zeolite was highest. The adsorption capacities of CO_2 in the studied zeolites were up to 38 times higher than those of CH_4. Diffusion constants of CO_2 and CH_4 decreased with an increase in the adsorbed amount and Na^+ number. Considering the adsorbed amount, adsorption selectivity and affinity, zeolites JSR with a low Na^+ number (JSR and Na_2JSR) is a good candidate for a pressure swing adsorption in the separation of CO_2/CH_4 mixture whereas JSR zeolites with high Na^+ ratios (Na_{16}JSR and Na_8JSR) may be a better selection for a vacuum swing adsorption.

Keywords Adsorption · CO_2 and CH_4 separation · GCMC method · Modified JSR zeolite

1 Introduction

Separation of CH_4 and CO_2 mixtures is a challenging research topic due to environmental and economic concerns. Several separation technologies have been introduced for CH_4 and CO_2 mixtures (Singh et al. 2009; Scholes et al. 2012; Kim et al. 2006). Due to excellent separation and energy efficiency, adsorptive processes have been widely studied for post-combustion CO_2 capture (Ebner and Ritter 2009), biogas purification (Alonso-Vicario et al. 2010), and the purification of coal mine methane and coal mine ventilation air (Olajossy et al. 2003; Lee et al. 2013). In the adsorptive cyclic processes, the adsorbent is a decisive factor for process feasibility and separation cost. According to many previous reports (Ackley et al. 2003; Yang et al. 2012; Ju et al. 2015; Mofarahi and Gholipour 2014), zeolites are considered as potential adsorbents for the separation of CH_4 and CO_2 mixtures.

Zeolites are crystalline, microporous materials with a large surface area and a molecular- sized pore structure. To date, more than 200 types of zeolites were reported, and each year a few new zeolites are distributed from IZA-SC

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(Structure Commission of the International Zeolite Association). The extra-framework cations in zeolites play a significant role in determining their adsorptive behaviors (Sebastian et al. 2007). Therefore, zeolites are commercially and widely applied to the fields of separation, purification, ion exchange and catalysis. However, there are inherent difficulties in quickly and intuitionally evaluating the adsorption behavior and capacity on new-issued zeolites.

In this study, JSR and Na_nJSR (modified JSR with Na^+), the newly issued zeolites, were selected as candidate adsorbents for the separation of CO_2 and CH_4 mixture. And the Grand Canonical Monte Carlo (GCMC) simulation was employed to understand the adsorption behaviors of CO_2 and CH_4 on JSR and Na_nJSR up to 1000 kPa. Then, the influence of Si/Al ratios and the Na^+ number on the adsorption behaviors of CO_2 and CH_4 was determined by four types of zeolite JSR (JSR, Na_2JSR, Na_8JSR and $Na_{16}JSR$). The results can contribute to selecting a proper adsorbent for effective gas separation processes.

2 Computational methods

2.1 Zeolite structures

In the study, a model of the silica JSR constructed in Xu's group was used for the selected JSR zeolites (Xu et al. 2013). The zeolite structure is described in Pa-3 space group. The crystal parameters are $a = 1.9845$ nm, $b = 1.9845$ nm, $c = 1.9845$ nm, $\alpha = 90°$, $\beta = 90°$, and $\gamma = 120°$.

The box in the simulation contained 8 unit cells (2 × 2 × 2) of the zeolite JSR. To construct the framework of Na_nJSR with a certain Si/Al ratio, Si atoms were partially substituted by Al atoms, and Na cations were added into the cell to compensate for the total charge to zero. Framework structures with various Si/Al ratios were obtained by replacing different numbers of Si atoms with Al atoms in the simulation box. For example, the Si/Al molar ratio of Na_2JSR with ten Al atoms in a simulation box was about 47. The structures of zeolites Na_nJSR with various Si/Al ratios were optimized by the energy minimization method to search for a conformational space of low energy structures. This method can provide not only reasonable configurations of Na_nJSR but also appropriate positions of all Na^+ ions. The structural properties for the simulation box of Na_nJSR are listed in Table 1.

Table 1 Structural properties for the simulation box of four zeolites JSR and Na_nJSR

Zeolite	n (Si)	n (Al)	Si/Al	n (O)	n (Na^+)
JSR	96	0	∞	192	0
Na_2JSR	94	2	47	192	2
Na_8JSR	88	8	11	192	8
$Na_{16}JSR$	80	16	5	192	16

2.2 Simulation techniques

The Grand Canonical Monte Carlo (GCMC) method was employed in this work, which is widely applied in the field of adsorption (Metropolis et al. 1953). The GCMC method used a grand canonical ensemble, in which the chemical potential of each species, the volume of system and the temperature were fixed (Agnihotri et al. 2008; Biswas and Cagin 2010). It was reported that the simulation reasonably predicted the experimental data (Rahmati and Modarress 2013; Nugent et al. 2013). In the present work, each zeolite framework was considered to be rigid. All the interactions of gas-zeolite and gas–gas were modeled using the PCFF force field (Hill and Sauer 1994; Sun 1995), which had been proved as a powerful force field to simulate adsorption in various zeolite systems (Song et al. 2002; Yang et al. 2008; Zhao et al. 2012).

The cut-off distance for the calculation of van der Waals potential energy was taken as 1.3 nm based on the atom-based technique. The partial charges of atoms were estimated by the charge-equilibration method (Rappe and Goddard 1991), and the electrostatic energy was calculated using the Ewald summation method (Karasawa and Goddard 1989) with an accuracy of 0.0001 kcal mol^{-1}. The partial pressure for describing the chemical potential of adsorbed molecules was calculated by using an ideal gas law.

In the GCMC simulation, adsorbate molecules in the zeolites were translated, rotated, created and deleted from the zeolite framework at a random with a probability of 0.225, 0.225, 0.275 and 0.275, respectively (Rahmati and Modarress 2009; Rahmati et al. 2012). For every state, 1×10^7 configurations were generated. The first 5×10^6 steps were used to achieve equilibration, and the last 5×10^6 steps were utilized to calculate the required adsorption properties. Periodic boundary conditions were applied to three-dimensions in order to simulate a definite system. Further details of the GCMC method can be found in the previous study (Dubbeldam et al. 2004a, b).

In this study, the diffusion of CO_2 and CH_4 on each JSR was also simulated using Newton's equations of motion until the average properties of the system did not change with time. Molecular dynamics (MD) simulations with the canonical (*NVT*) ensemble and periodic boundary conditions were performed to study the diffusion behaviors of CO_2 and CH_4 in the selected zeolites using a Forcite module in the Materials Studio. During the initializing period, an *NVT* MC simulation was utilized to rapidly achieve an equilibrium molecular arrangement. After the initialization step, the velocities of pseudo-atoms from the Boltzmann distribution were assigned at the desired average temperature. The total momentum of the system was set to zero. Then, the *NVT* MD simulation was further carried out for the system using the Nose–Hoover thermostat (Martyna et al. 1996). In the MD simulation, a simulation time step of 1.0 fs was employed, which was sufficiently small to ensure good energy conservation. 200 ps was initially allowed for the equilibrium of system and was followed by 400 ps in *NVT*-MD simulation. And the trajectories were saved every 1000 steps for further analysis.

The mean square displacement (MSD) obtained from the simulation works, the self- diffusivities (*D*), was applied to the analysis with the following Einstein equation:

$$D = \lim_{t \to \infty} \frac{1}{6N_a t} < \sum_{i=1}^{N_a} [r_i(t) - r_i(0)]^2 >$$

In this equation, N_a represents the number of molecules of species i and $r_i(t)$ is the position of species i at a time t.

3 Results and discussion

3.1 Comparisons with experimental data

For the verification of the simulation techniques used, the adsorption isotherms of CO_2 and CH_4 in the zeolite MFI were compared with the experimental data (Babarao et al. 2007; Krishna and van Baten 2007; Zhu et al. 2006; Golden and Sircar 1994). As shown in Fig. 1, a good agreement between the simulation results and experimental isotherms was observed. It implied that the simulation method in the study was feasible for evaluating and estimating the adsorption behaviors of CO_2 and CH_4 on purely siliceous zeolites. Therefore, the simulation method was applied to the CO_2 and CH_4 adsorption in the zeolites JSR and Na_nJSR in the study.

3.2 Adsorption of CO_2 and CH_4

Adsorption isotherms of CO_2 and CH_4 in JSR, Na_2JSR, Na_8JSR and Na_{16}JSR at 298 K were presented in Fig. 2. After the CO_2 adsorption isotherms of the zeolites Na_nJSR with high Na^+ ratios (Na_8JSR and Na_{16}JSR) increased steeply at a low pressure range (<150 kPa), it approached asymptotically equilibrium saturation. On the other hand, the adsorption isotherms of JSR and Na_2JSR were much lower than those of Na_8JSR and Na_{16}JSR at a low pressure range, showing small curvature in an isotherm shape.

At a low pressure range (<150 kPa), the adsorption amount became higher with an increase in Na^+ ratio. However, the difference between Na_8JSR and Na_{16}JSR was minute. Furthermore, the isotherms of both adsorbents showed a crossover with further increase in pressure. The crossover of isotherms between JSR and Na_2JSR was also observed at approximately 500 kPa. In addition, the adsorption amount of CO_2 at a high pressure range (>850 kPa) became higher in the JSRs with a low Na^+ number due to the crossover of both isotherms.

As shown in Fig. 2b, the isotherms of CH_4 was much lower than the corresponding isotherms of CO_2, showing almost a linear shape. The adsorption amount became smaller in the whole pressure range as the Na^+ number increased. And the difference in the CH_4 isotherms between Na_8JSR and Na_{16}JSR was relatively larger than that of CO_2.

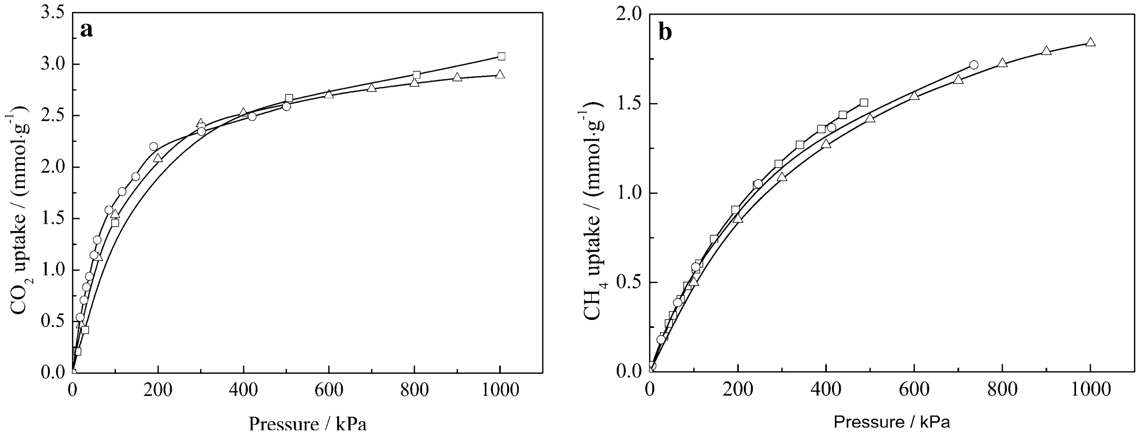

Fig. 1 The adsorption isotherms of CO_2 and CH_4 in purely siliceous zeolite MFI: **a** CO_2 (*square*), literature data from (Babarao et al. 2007), 300 K (*circle*), literature data from (Krishna and van Baten 2007), 303 K (*triangle*), this work, 298 K. **b** CH_4 (*square*), literature data from (Zhu et al. 2006), 303 K (*circle*), literature data from (Golden and Sircar 1994), 304 K (*triangle*), this work, 300 K

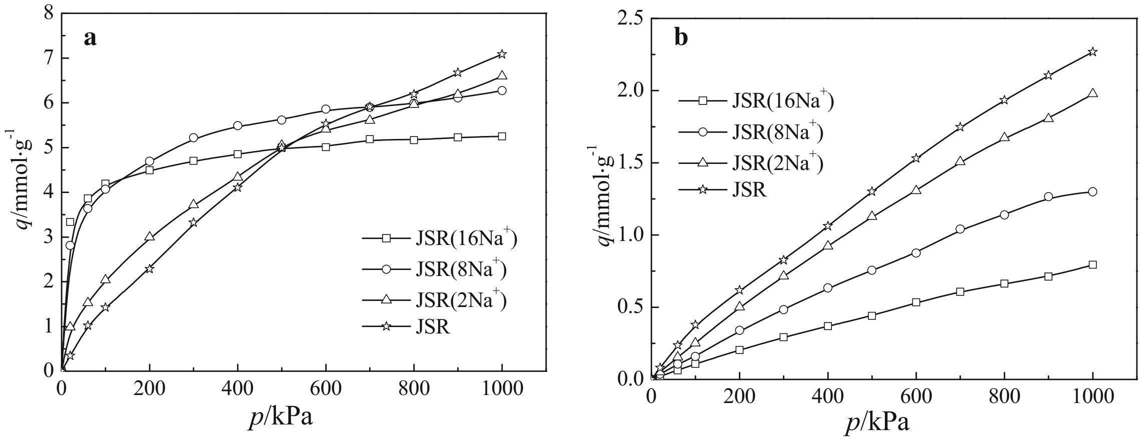

Fig. 2 Adsorption isotherms of CO_2 and CH_4 in JSR and Na_nJSR at 298 K: **a** CO_2 and **b** CH_4

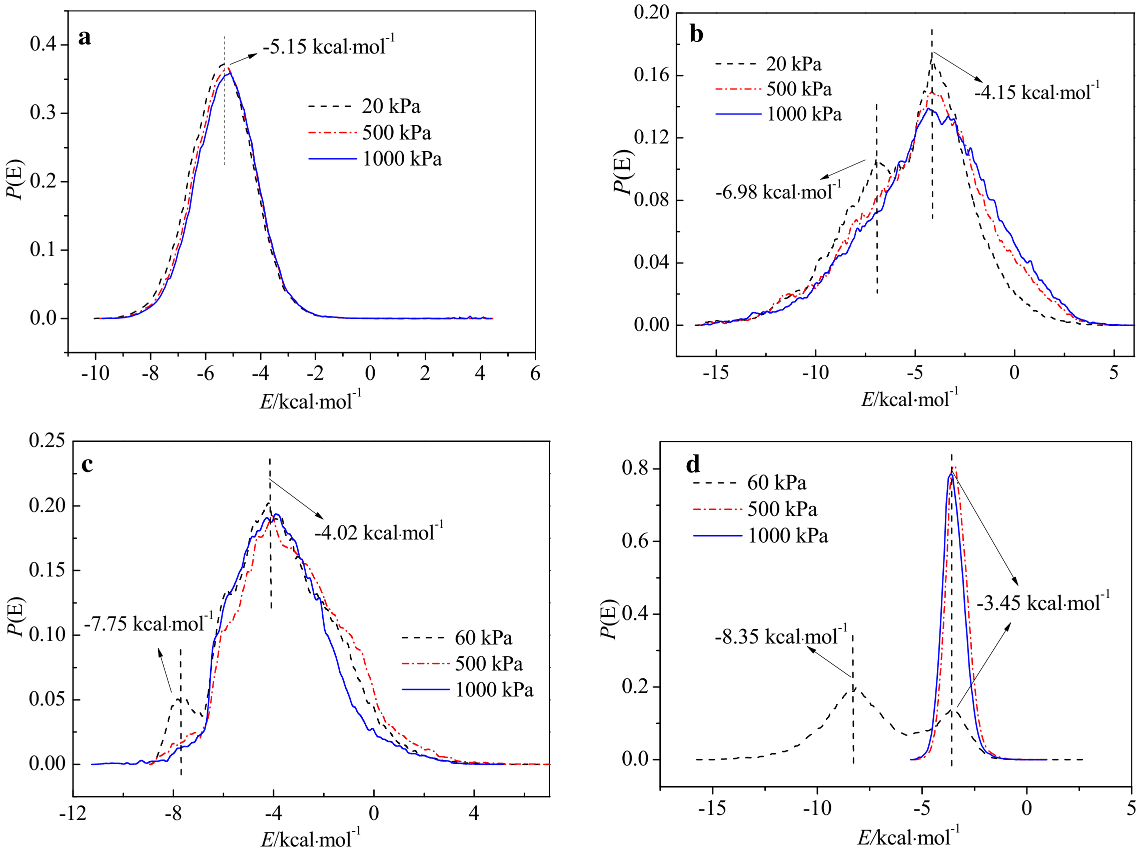

Fig. 3 Adsorption energy of CO_2 in JSR and Na_nJSR at different pressures at 298 K: **a** JSR, **b** Na_2JSR, **c** Na_8JSR and **d** $Na_{16}JSR$

CO_2 molecules yield a large quadrupole. Moreover, the polarity of C–O bond and lone pairs of electrons of oxygen atoms produce strong electrostatic interaction with Na^+ in the zeolite framework. In addition, the two energy peaks of the adsorption interaction curves between CO_2 and Na_nJSR in Fig. 3 imply that Na^+ ions in Na_nJSR also creates extra active adsorption sites at a low pressure. Therefore, the adsorbed amount increased with the Na^+ number in the CO_2 adsorption.

However, it is noted that the sequence of the CO_2 amount adsorbed at a high pressure range (>850 kPa) was opposite to those at a low pressure range due to the steric effect of the Na^+ ions occupied in the zeolite structural space (Siriwardane et al. 2003; Zhang et al. 2014). The

Table 2 Free volumes of zeolites with different Si/Al ratios

Zeolite	Si/Al	*n* (Na^+)	Free volume (cm^3/kg)	V_i/V_{JSR} (%)
JSR	∞	0	480.17	
Na_2JSR	47	2	462.97	96
Na_8JSR	11	8	412.99	86
$Na_{16}JSR$	5	16	347.36	72

volume effect of Na^+ on adsorption could be quantified by the free volume characterization of the zeolites, which were analyzed by the Connolly surface method (Connolly 1985). The probe molecule selected was the hard spheres with a radius of 0.1 nm and the simulated results for the free volume are summarized in Table 2. The free volume became small with a decrease in the Si/Al ratio or an increase in the Na^+ numbers

In the case of CH_4 adsorption, CH_4 molecules with a tetrahedral structure have a weak electrostatic interaction with Na^+ in a zeolite framework (Qian et al. 2011), and the steric effect of Na^+ on CH_4 adsorption caused a decrease in the adsorbed amount. No extra active adsorption sites between CH_4 and Na_nJSR appeared in Fig. 4. It implies that the contribution of Na^+ ions to CH_4 adsorption is not significant. According to the comparison of the adsorption energy between CH_4 and CO_2 in different zeolites Na_nJSR as shown in Figs. 3 and 4, the adsorption process is exothermic, but the adsorption affinity of CO_2 is much higher than that of CH_4. And the extra peak intensity of the adsorption energy turned weaker when the pressure became higher.

Table 3 shows that the adsorption capacities of CO_2 in these zeolites are up to 38 times higher than those of CH_4 in terms of the ratios of equilibrium adsorption capacity. Equilibrium selectivity between CO_2 and CH_4 increased with an increase in Na^+ numbers, while it decreased with an increase in the adsorption pressure. Considering the adsorption capacity, selectivity and regeneration, the zeolites Na_8JSR and $Na_{16}JSR$ are good candidates for the separation of the CO_2/CH_4 mixture at vacuum swing adsorption processes because the interaction energy between CO_2 and $Na_{16}JSR$ is quite strong at a low pressure range. On the other hand, zeolites JSR and Na_2JSR are recommended for pressure swing adsorption processes when the feed pressure is relatively high due to the high adsorption capacity and relatively easy regeneration.

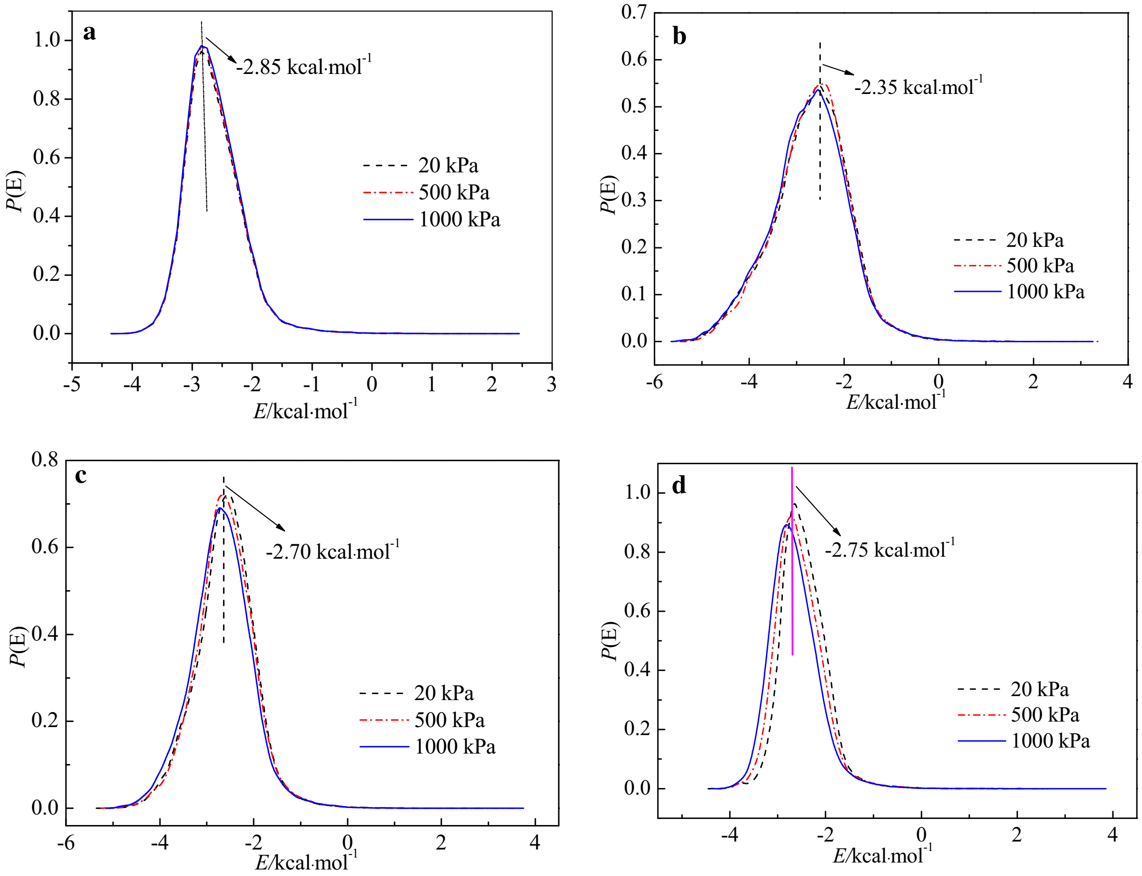

Fig. 4 Adsorption energy of CH_4 in JSR and Na_nJSR at different pressures at 298 K: **a** JSR, **b** Na_2JSR, **c** Na_8JSR and **d** $Na_{16}JSR$

3.3 Prediction of adsorption isotherms

Adsorption isotherms of CO_2 and CH_4 on zeolites JSR and Na_nJSR were fitted with the Langmuir Eq. (1) and Freundlich Eq. (2), respectively.

$$q = q_m \frac{bp}{1 + bp} \tag{1}$$

$$q = kp^n \tag{2}$$

Table 3 Adsorption amount ratios between CO_2 and CH_4 on JSR and Na_nJSR at different pressures

Zeolite	Adsorption amount (q/mmolg^{-1})	100 kPa	R	300 kPa	R	500 kPa	R	900 kPa	R
JSR	$q(CO_2)$	1.43	4.1	3.27	3.9	4.99	3.8	6.68	3.2
	$q(CH_4)$	0.35		0.84		1.30		2.10	
Na_2JSR	$q(CO_2)$	2.08	8.0	3.76	5.3	4.99	4.4	6.24	3.4
	$q(CH_4)$	0.26		0.71		1.13		1.81	
Na_8JSR	$q(CO_2)$	4.07	25.4	5.19	10.8	5.64	7.5	6.15	4.9
	$q(CH_4)$	0.16		0.48		0.75		1.25	
Na_{16}JSR	$q(CO_2)$	4.18	38.0	4.69	16.2	4.99	11.3	5.24	7.4
	$q(CH_4)$	0.11		0.29		0.44		0.71	

R CO_2/CH_4 adsorption amount ratio

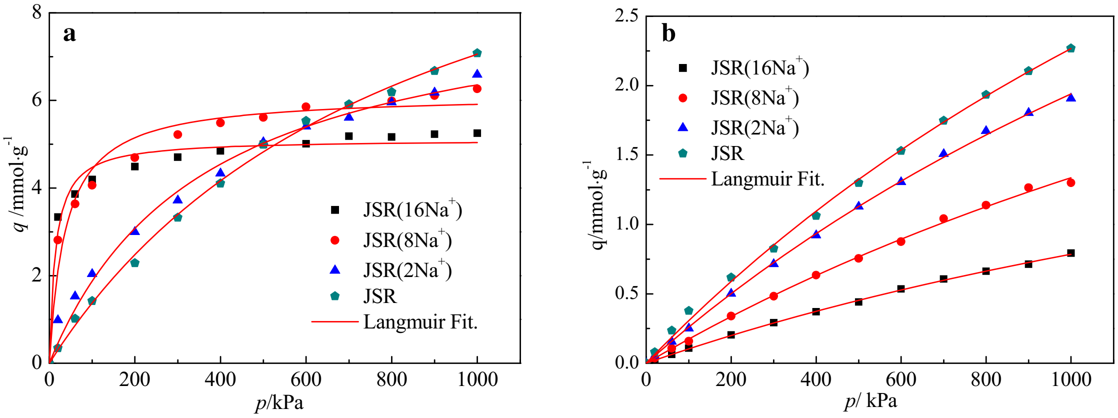

Fig. 5 Fitting curves of CO_2 and CH_4 on zeolites with Langmuir equation: **a** CO_2 and **b** CH_4

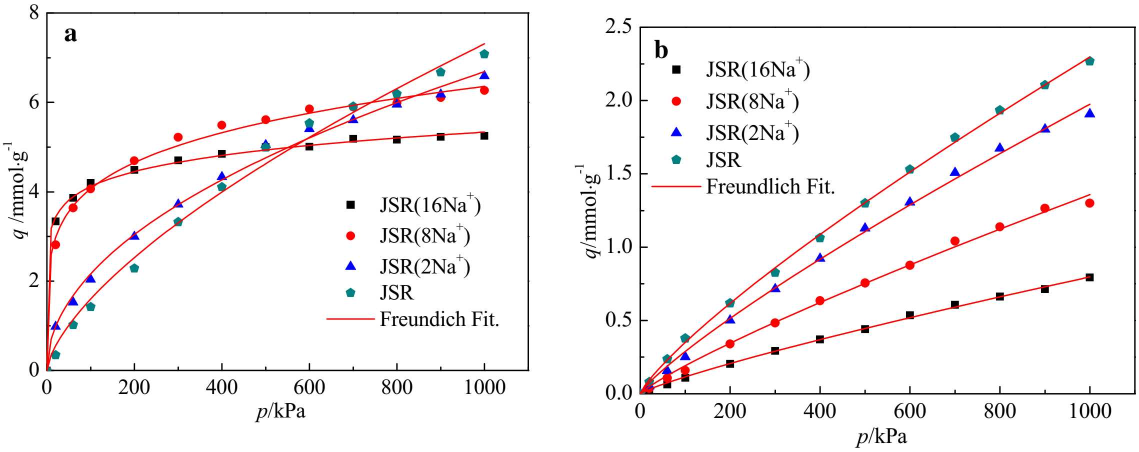

Fig. 6 Fitting curves of CO_2 and CH_4 on zeolites with Freundlich equation: **a** CO_2 and **b** CH_4

Table 4 Parameter values of adsorption isotherms predicted by Langmuir and Freundlich equations

Zeolite	Langmuir parameters					Freundlich parameters				
	CO_2		R^2	CH_4	R^2	CO_2		R^2	CH_4	R^2
JSR	q_m	13.11	0.998	7.87	0.998	k	0.077	0.993	0.00815	0.999
	b	0.0012		4.04×10^{-4}		n	1.515		1.224	
Na_2JSR	q_m	8.66	0.989	6.88	0.999	k	0.227	0.996	0.00613	0.999
	b	0.0028		3.92×10^{-4}		n	2.041		1.196	
Na_8JSR	q_m	6.14	0.967	5.21	0.998	k	1.664	0.996	0.00378	0.997
	b	0.0260		3.45×10^{-4}		n	5.152		1.173	
$Na_{16}JSR$	q_m	5.11	0.976	2.94	0.999	k	2.451	0.998	0.00213	0.998
	b	0.0701		3.64×10^{-4}		n	8.880		1.162	

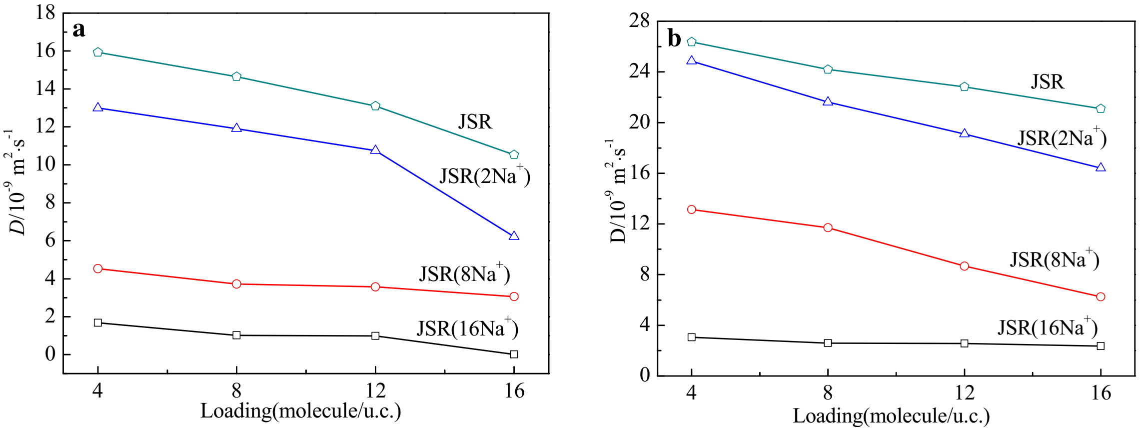

Fig. 7 Self-diffusion coefficients of pure CO_2 and CH_4 as a function of the loading on Na_nJSR at 298 K: **a** CO_2 and **b** CH_4

Where q is adsorption amount, mmol/g; q_m denotes saturated adsorption amount, mmol/g; p represents adsorption pressure,kPa; b and n are Langmuir constant and Freundlich constant, respectively; k is a constant correlated with the characteristics between adsorbents and adsorbates.

The predicted results are shown in Figs. 5 and 6, and the fitting parameters are listed in Table 4. The experimental adsorption isotherms were well fitted with the Langmuir and Freundlich isotherms, but the Freundlich isotherms were slightly better than the Langmuir isotherms. As can be expected from Figs. 3 and 4, the affinity constant, b or n, between CO_2 and zeolite Na_nJSR increased with the number of Na^+ in Table 4, which indicated increased adsorption affinity with an increase in the Na^+ number. However, the difference of affinity constant, b or n, between CH_4 and zeolite Na_nJSR was small, which demonstrated a minute contribution of Na^+ in zeolite Na_nJSR to the adsorption of CH_4.

3.4 Diffusion constants

According to the simulation method mentioned above, the diffusion constants of CO_2 and CH_4 on JSR, Na_2JSR, Na_8JSR and $Na_{16}JSR$ zeolites at 298 K are presented in Fig. 7. The results denoted that their diffusion constants decreased with an increase in the adsorption amount and the Na^+ number. Furthermore, the diffusion of CH_4 was faster than that of CO_2 in the same zeolite. The variation of the diffusion constant of CO_2 on Na_8JSR and $Na_{16}JSR$ zeolites with a loading amount was minute. However, the small variation of the diffusion constant was only observed at $Na_{16}JSR$ in CH_4 adsorption, and the difference of diffusion between JSR and $Na_{16}JSR$ zeolites was much higher than that in the CO_2 adsorption. The phenomena stemmed from the relatively high interaction energy of adsorbate molecules and steric effect of Na^+ in the CO_2 adsorption.

4 Conclusions

The GCMC techniques were employed to simulate adsorption behaviors of CO_2 and CH_4 in zeolites JSR and Na_nJSR. The adsorption isotherms of CO_2 and CH_4 in zeolites JSR and Na_nJSR were obtained from the constructed frameworks of the zeolites with various Si/Al ratios.

The pore volume of the zeolites played important roles in the adsorption behaviors, and they decreased with an increase in the Na^+ number. The adsorption amount of CO_2 was higher with the Na^+ number at a low pressure range (<150 kPa). However, the result became opposite as in the Na^+ number increased at a high pressure range (>850 kPa). CO_2 was adsorbed on two active sites in the zeolites because two energy peaks were observed from the interaction energy curves. CO_2 isotherms on Na_8JSR and $Na_{16}JSR$ reached adsorption saturation at a relatively low pressure range after showing a steep increase of the isotherms with pressure. On the other hand, the adsorption amount of CH_4 became smaller with an increase in the Na^+ number and only one energy peak was observed. It implied that introduction of more Na^+ was not beneficial to CH_4 adsorption. Adsorption energy indicated that the adsorption process was exothermic, but extra peak intensity of the CO_2 adsorption energy turned weak with increasing pressure.

Adsorption isotherms of CO_2 and CH_4 were well fitted with the Langmuir and Freundlich equations, showing slightly better results in the Freundlich isotherms. The adsorption capacities of CO_2 in these zeolites were up to 38 times larger than those of CH_4 based on the ratios of the equilibrium adsorption capacity. Diffusion constants of CO_2 and CH_4 in the zeolites decreased with an increase in the adsorption amount and the Na^+ number. Considering the adsorption affinity, capacity and selectivity, zeolites JSR with a low Na^+ number (JSR and Na_2JSR) can be regenerated by a pressure swing in a cyclic adsorptive process for the separation of CO_2/CH_4 mixture. And JSR zeolites with a high Na^+ number ($Na_{16}JSR$ and Na_8JSR) may need a vacuum for regeneration because of the strong adsorption affinity of CO_2 under high CO_2/CH_4 selectivity.

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