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Adsorption and separation of carbon dioxide and methane in new zeolites using the Grand Canonical Monte Carlo method

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Abstract The adsorption and separation behaviors of CO_2 and CH_4 in new siliceous zeolites (IFO, JSR, OKO, SEW) were simulated using the Grand Canonical Monte Carlo method in the paper. The adsorption isotherms for pure components and binary mixtures of CO_2 and CH_4 in four siliceous zeolites were obtained. The adsorption thermodynamic properties including Gibb's free energy change, enthalpy change and entropy change were investigated. The results demonstrate that the adsorbed amount of pure components increases with an increase in pressure, and larger pore volume and surface area are beneficial to improve the adsorption capacity. The adsorption amount of CO_2 and CH_4 in the JSR zeolite is 7.08 and 2.27 mmol g^{-1} at 1000 kPa, respectively. In view of the thermodynamic results, the new siliceous zeolites show a higher affinity for CO_2. The adsorption capacities of CO_2 in all zeolites were five times more than those of CH_4 in binary mixtures based on the ratios of equilibrium adsorption capacity. Considering the adsorption uptake and selectivity for CO_2/CH_4, the JSR zeolite is a good candidate for the separation of CO_2/CH_4 at low pressure.

Keywords Adsorption · Separation · GCMC method · Zeolite · CO_2/CH_4

1 Introduction

Separation of CH_4 and CO_2 mixtures is a challenging research topic due to environmental and economic concerns, and the inherent difficulties in conducting experiments. There are several technologies applied for the separation of mixtures of CH_4 and CO_2 (Singh et al. 2009; Scholes et al. 2012), in which adsorption-based processes are widely used for post-combustion CO_2 capture (Ebner and Ritter 2009), the purification of biogas (Alonso-Vicario et al. 2010), and the purification of coal mine methane and coal mine ventilation air (VAM) (Olajossy et al. 2003). The reason is that the separation cost is usually low if the separation is based on the difference of components in adsorption (Ruthven et al. 1994). Furthermore, the adsorbent is a decisive factor of feasibility and separation cost. In a cost-effective manner, zeolites are considered as potential sorbents for the adsorption of CH_4 and CO_2 gas mixtures (Ackley et al. 2003; Yang et al. 2012; Zhang et al. 2012; Mofarahi and Gholipour 2014).

Zeolites have been intensively investigated in recent decades because of their large surface areas and molecular sized porous structures (Zhang et al. 2014; Dunne et al. 2009; Bakhtyari and Mofarahi 2014). They are an

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important class of materials in which separations are obtained by selecting the pore size such that in mixtures molecules that are too large are blocked (Smit and Maesen 2008). Therefore, zeolites are widely used in applications such as separation, purification, ion exchange, catalysis and the isolation of biological molecular (Krishna and van Baten 2005; Rouleau et al. 2009). Currently, about 200 types of zeolite have been crystallographically classified and several new types still appear every year (Liu et al. 2013). Thus, studies on the adsorption and separation behaviors for CH_4 and CO_2 mixtures in new zeolites are very important and attractive from the viewpoints of science and their applications.

However, zeolites are also challenging because it is very difficult to carry out experiments that provide us with information at the molecular level. In this respect, molecular simulations nicely complement experiments (Catlow et al. 2004). With the development of computer technology, molecular simulation methods, such as Grand Canonical Monte Carlo (GCMC), are playing an important role in developing our understanding of the relationship between the microscopic and macroscopic properties of molecular fluids confined in zeolites, and can be used to generate adsorption isotherms for gases on microporous solid adsorbents (Liu et al. 2011; Kim et al. 2013). To date, the adsorption of water/methanol and water/ethanol mixtures in zeolite 4A was simulated using the GCMC simulation (Wu et al. 2009). The Cosoli group (Cosoli et al. 2008b) studied H_2S removal from biogas streams using different zeolites such as NaX, NaY, LTA and MFI with the GCMC method. Pham et al. (Pham et al. 2014) studied the adsorption of N_2 and CO_2 in pure silica zeolites (BEA, CHA, FER, MFI, and STT) experimentally and by GCMC simulation, and the agreement between computed adsorption isotherms and isosteric heats with those found experimentally was excellent. The Calero group investigated the adsorption selectivity of CO_2, N_2 and CH_4 in MFI, MOR, ISV, ITE, CHA and DDR (García-Pérez et al. 2007). The results showed that the selectivity behavior strongly depended on the type of material structure and the bulk composition of the mixture. Therefore, molecular simulations have become a powerful tool to explore both materials science and life science fields (Zeng et al. 2007; Cosoli et al. 2008a).

In this work, the adsorption and separation properties for CO_2 and CH_4, and the selectivity performance of new siliceous zeolites (IFO, JSR, SEW and OKO) were investigated using the molecular simulation method, which would quickly aid in choosing effective adsorbents for gas adsorption and separation, and could be practically important for gas separation from low-concentration mine gas.

2 Computational methods

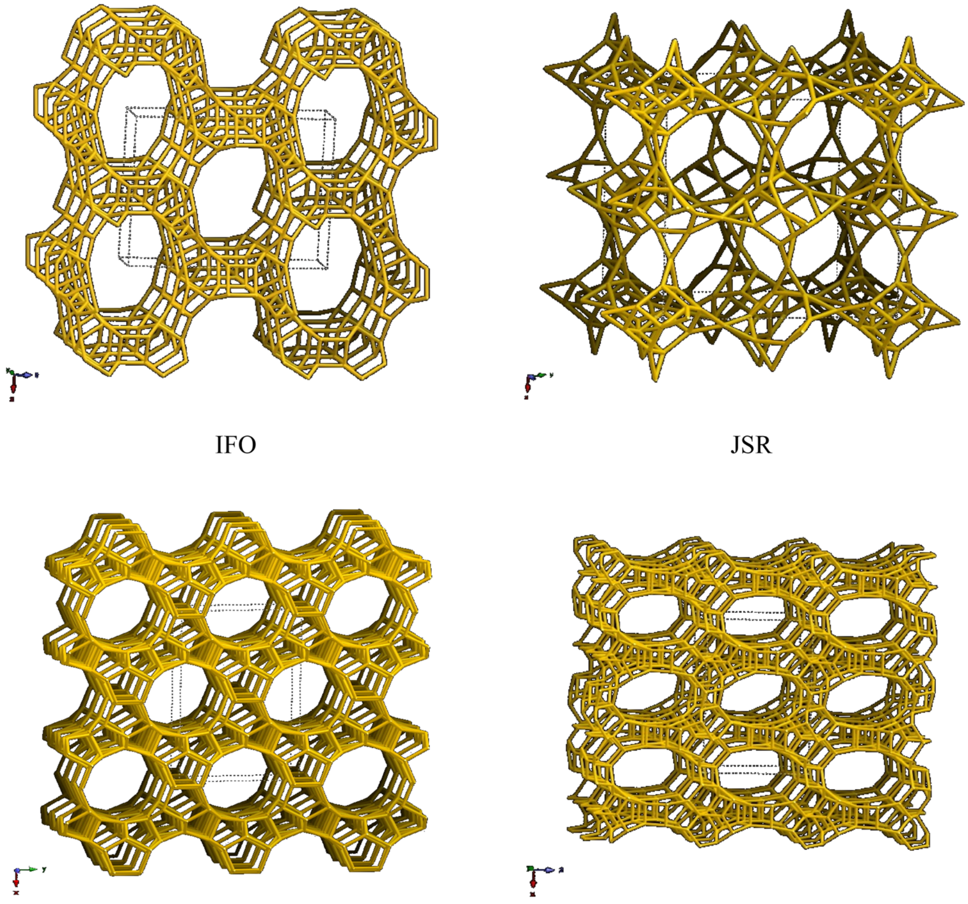
2.1 Zeolite structures

New zeolites are discovered and synthesized annually. Their adsorption, separation and selectivity properties are worth investigating and can be a fascinating area of research. Therefore, the separation of CO_2 and CH_4 in four new siliceous zeolites (IFO, JSR, OKO and SEW) was investigated using the GCMC method. Framework structures of the new siliceous zeolites are shown in Fig. 1, and details of the different zeolite structures used in the calculations are listed in Table 1 (Martinez-Franco et al. 2013; Xu et al. 2013; Verheyen et al. 2012; Xie et al. 2011).

2.2 Simulation techniques

The Grand Canonical Monte Carlo (GCMC) method was employed in this work (Metropolis et al. 1953), which is widely applied in the study of adsorption problems. The GCMC method uses a grand canonical ensemble, in which the chemical potential of each species, the volume of the system and the temperature are fixed (Agnihotri et al. 2008; Biswas and Cagin 2010). Hence, comparisons between simulation results and experimental data are reasonable because the adsorption conditions (pressure and temperature) are also constant in the experiments (Rahmati and Modarress 2013; Nugent et al. 2013).

In the present work, each zeolite framework was considered to be rigid. All interactions of gas–zeolite and gas–gas were modeled using the PCFF force field (Hill and Sauer 1994; Sun 1995). The PCFF has been proved as a powerful force field supporting for adsorption in many zeolite systems (Song et al. 2002; Yang et al. 2008; Zhao et al. 2012). The cutoff distance for the calculation of the van der Waals potential energy by an atom based technique was taken as 1.3 nm. 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 required for describing the chemical potential of the adsorbed molecules was calculated using the ideal gas law. In the GCMC simulation, adsorbate molecules in the zeolite were translated, rotated, created and deleted from the zeolite framework at 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 used for calculation of the



IFO JSR

OKO SEW

Fig. 1 Framework structures of new siliceous zeolites

Table 1 Structural properties of new zeolites

Zeolite type	Composition	Unit cell volume (Å)	Space group	Simulation cell size (a × b×c)
IFO	$Si_{32}O_{64}$	$a = 16.4388$ $b = 4.9453$ $c = 22.7830$	Pnmm	2 × 6×2
JSR	$Si_{96}O_{192}$	$a = 19.8450$ $b = 19.8450$ $c = 19.8450$	Pa-3	2 × 2×2
OKO	$Si_{68}O_{136}$	$a = 24.0638$ $b = 13.8332$ $c = 12.3516$	C12/m1	2 × 2×3
SEW	$Si_{66}O_{132}$	$a = 23.7289$ $b = 11.2932$ $c = 14.4719$	Pmmn	2 × 3×2

required properties and subsequent data analysis. For the MFI-type zeolite, the supercell consists of 8 unit cells ($2 \times 2 \times 2$, $a = 2.007$ nm, $b = 1.992$ nm and $c = 1.342$ nm). Periodic boundary conditions were applied in three-dimensions in order to simulate an infinite system. Further details of the GCMC method can be found in the literature (Dubbeldam et al. 2013).

3 Results and discussion

3.1 Comparisons with experimental data

To verify the simulation techniques, the adsorption isotherms of CO_2 and CH_4 in the MFI zeolite were compared to experimental data (Babarao et al. 2007; Krishna and van

Baten 2007; Zhu et al. 2006; Golden and Sircar 1994), as shown in Fig. 2. A good agreement between the simulation results and experimental data was found based on the adsorption isotherms, which demonstrated that the simulation techniques were satisfactory for the simulation of CO_2 and CH_4 adsorption in purely siliceous zeolites. Therefore, the simulation techniques were applied in the adsorption studies for CO_2 and CH_4 in the IFO, JSR, OKO and SEW zeolites.

3.2 Adsorption of CO_2 and CH_4 in new siliceous zeolites

Adsorption isotherms for CO_2 and CH_4 in the four zeolite structures at 298 K are shown in Fig. 3. The results show that the adsorbed amount of each pure component increases with an increase in pressure, and the sequence for the adsorption amount of CO_2 and CH_4 in these zeolites is JSR > SEW > OKO > IFO. The adsorption amount of CO_2 and CH_4 adsorbed in the JSR zeolite is 7.08 and 2.27 mmol g^{-1} at 1000 kPa, respectively. Comparing with NaX, NaY, MFI, CHA and DDR zeolites, the adsorption amount of CO_2 is higher than that in NaX, NaY, CHA or DDR, whereas the adsorption amount of CH_4 is smaller than that in these zeolites, and the adsorption amount of CO_2 and CH_4 in the MFI zeolite is only 2.89 and 2.05 mmol g^{-1} at 1000 kPa (Zhang et al. 2014; Krishna et al. 2006). On the other hand, for RWY, STW, SOF, PUN, STO, SSF, LTF, IWS, ITR, SVR, BSV and SFS zeolites (Rahmati and Modarress 2013), the maximum adsorption amount of CO_2 and the minimum adsorption amount of CH_4 in the these zeolites is 3.78 and 1.36 mmol g^{-1} at 1000 kPa, respectively. Thus, JSR zeolite is a better adsorbent for the separation of CO_2 and CH_4 mixture among these zeolites because it has higher CO_2 adsorption amount and equilibrium adsorption amount ratio between CO_2 and CH_4. The adsorption capacity for CO_2 is higher than that of CH_4 in all the zeolites under the same conditions because CO_2 is a more slender molecule than CH_4 and the energy barrier for inter-cage hopping is lower than that for CH_4 (Krishna et al. 2006). Therefore, the steric hindrance in the CH_4 molecule is greater than that of CO_2 (Krishna and van Baten 2007). Further, CO_2 has higher affinity than CH_4 because CO_2 has quadrupole and the electrostatic potential of the quadrupole term is proportional to the electric charge of ions (Zhang et al. 2014).

The pore volume and surface area are very important parameters to understand the adsorption and diffusion behavior of penetrated molecules in nanoporous materials. In this work, the pore volume and surface area characterization of the zeolites were analyzed by the Connolly surface method (1985). The probe molecule was selected using hard spheres with a radius of 0.165 nm (the kinetic radius of CO_2). The simulated results for the pore volume and surface area were summarized in Table 2. As listed in Table 2, the magnitude of the pore volume and surface area can be ranked as follows: JSR > SEW > OKO > IFO, which is consistent with the adsorption capacity for CO_2 and CH_4. The result indicates that larger pore volume and surface area are beneficial to improve gas adsorption capacity in zeolites.

3.3 Adsorption thermodynamics

The adsorption process is always accompanied by changes in the system for Gibb's free energy, enthalpy and entropy, which are favorable to understand the adsorption mechanism and the interactions between adsorbents and

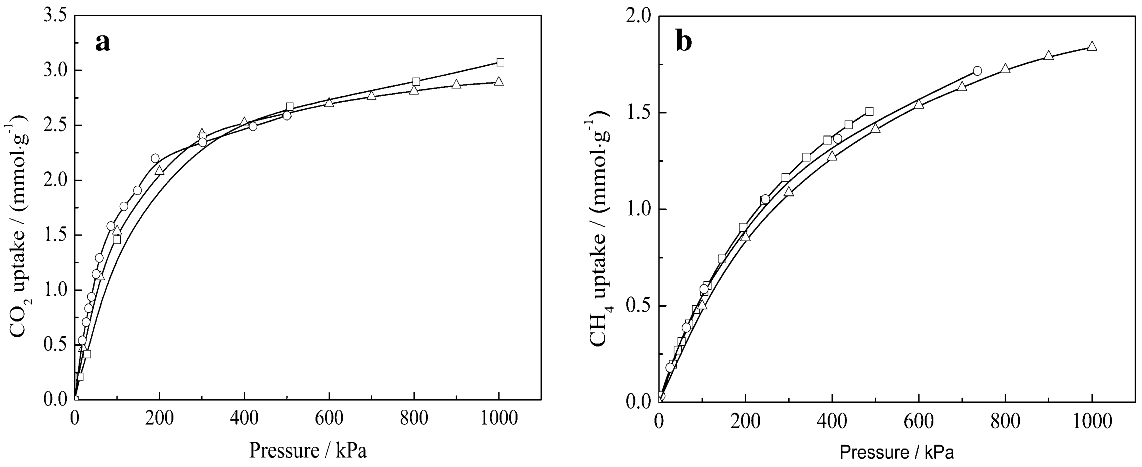


Fig. 2 The adsorption isotherms of CO_2 and CH_4 in purely siliceous zeolite MFI: (a) CO_2: *open square* literature data from Babarao et al. (2007), 300 K; *open circle* literature data from Krishna and van Baten (2007), 303 K; *triangle* this work, 298 K. (b) CH_4: *open square* literature data from Zhu et al. (2006), 303 K; *open circle* literature data from Golden and Sircar (1994), 304 K; *triangle* this work, 300 K

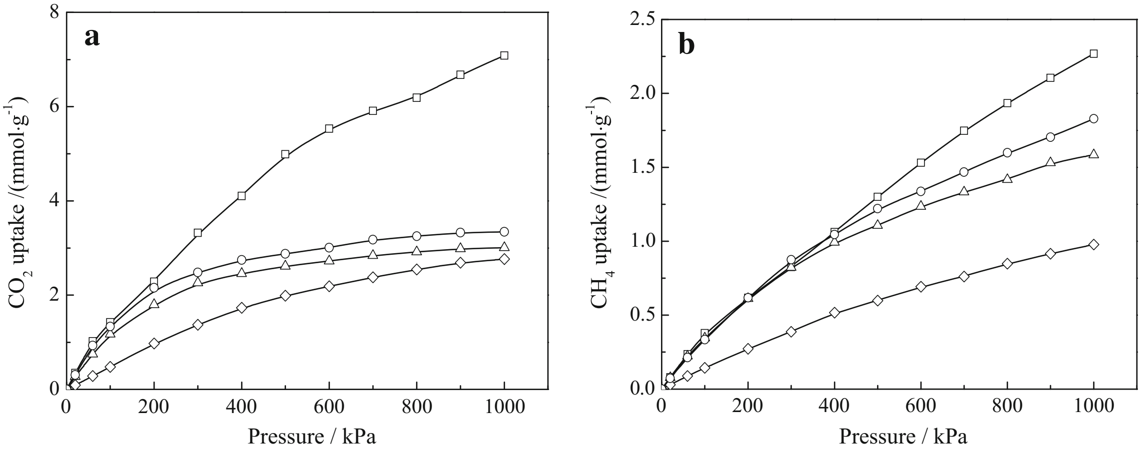


Fig. 3 The adsorption isotherms of CO_2 and CH_4 in new siliceous zeolites at 298 K (a) CO_2 (b) CH_4: *diamond* IFO zeolite; *open square* JSR zeolite; *triangle* OKO zeolite; *open circle* SEW zeolite

Table 2 The free volume and surface area of new siliceous zeolites

Zeolite type	Pore volume/unit cell (nm^3)	Surface area/unit cell (nm^2)
IFO	0.62	3.04
JSR	4.49	20.47
OKO	1.32	7.90
SEW	1.37	8.11

adsorbates. The thermodynamic parameters of Gibb's free energy change, ΔG^0, enthalpy change, ΔH^0, and entropy change, ΔS^0, for the adsorption process were calculated using the following equations:

$$\Delta G^0 = -RT \ln K, \tag{1}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0, \tag{2}$$

where K is the equilibrium constant, R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature in Kelvin. For Eqs. 1 and 2, the temperature dependent K is expressed as follows:

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}. \tag{3}$$

The equilibrium constant at zero coverage limit (Pham et al. 2014; Golden and Sircar 1994) for the pure components (CO_2 and CH_4) in the new siliceous zeolites over the temperature range from 273 to 348 K are shown in Fig. 4. The results show that the equilibrium constant decreases with an increase in temperature. Moreover, the K values for CO_2 are larger than those found for CH_4 at the same temperature.

The Gibb's free energy change, ΔG^0, calculated using Eq. 1 is plotted in Fig. 5. The Gibb's free energy change was found to be linear with temperature. An increase in temperature causes an increase in the ΔG^0 value, which indicates a lower temperature is advantageous for the adsorption process. The negative values of ΔG^0 suggest that the adsorption process is favorable and spontaneous for CO_2 and CH_4. In addition, the adsorption of CO_2 molecules was more favorable than that of CH_4 because the ΔG^0 values for CO_2 are more negative.

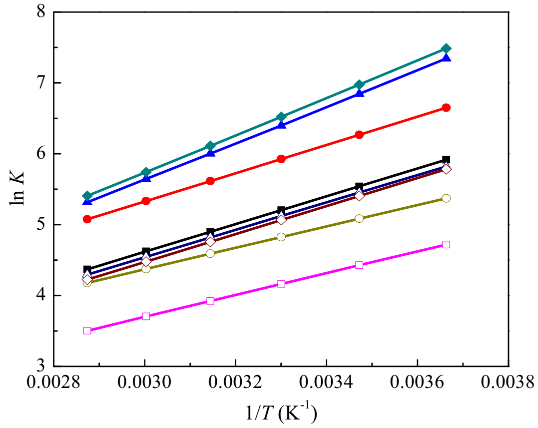


Fig. 4 Plot of the logarithm of the equilibrium constants ln$K$ versus 1/T: *filled square* IFO-CO_2; *filled circle* JSR-CO_2; *filled triangle* OKO-CO_2; *filled diamond* SEW-CO_2; *open square* IFO-CH_4; *open circle* JSR-CH_4; *open triangle* OKO-CH_4; *open diamond* SEW-CH_4

The results of the enthalpy change, ΔH^0 and entropy change, ΔS^0 can be estimated from the slope and intercept of the linear relationship in Eq. 3, and the results are

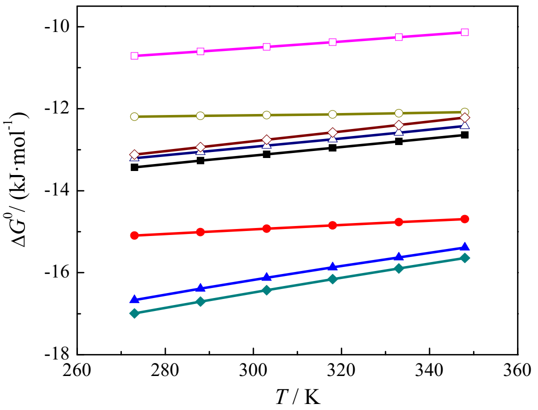


Fig. 5 Plot of Gibbs free energy change, ΔG^0, versus temperature T: *filled square* IFO-CO_2; *filled circle* JSR-CO_2; *filled triangle* OKO-CO_2; *filled diamond* SEW-CO_2; *open square* IFO-CH_4; *open circle* JSR-CH_4; *open triangle* OKO-CH_4; *open diamond* SEW-CH_4

presented in Table 3. As listed in Table 3, the new zeolites have a higher affinity to CO_2 according to the more negative enthalpy change for CO_2. The isosteric heat of adsorption, a commonly reported thermodynamic quantity, is given by $q_{st} = -\Delta H^0$ at the zero occupancy (Zhu et al. 2006; Talu and Myers 2001). Moreover, their isosteric heats of CO_2 adsorption are higher than that of CH_4, demonstrating the stronger binding capacity between CO_2 and zeolites (Colabella et al. 1988).

The negative adsorption entropy ΔS^0 for both CO_2 and CH_4 suggests that the adsorption of CO_2 and CH_4 molecules in four zeolites is in an ordered arrangement because the motion of gas molecules is transformed from the three-dimensional space into a two-dimensional space. Further, the less negative entropy of CH_4 when compared with CO_2 in each new zeolite indicates the increased randomness of CH_4 (Zhang et al. 2014). All simulated results for Gibb's free energy, enthalpy and entropy change, as well as the isosteric heat of adsorption are consistent and show that CO_2 is more favorable to be adsorbed than CH_4 in these four zeolites.

Table 3 Enthalpy change ΔH^0 and entropy change ΔS^0 for the adsorption of CO_2 and CH_4 in zeolites

Gas, zeolite	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1})
CO_2, IFO	−16.296	−10.600
CO_2, JSR	−16.552	−5.355
CO_2, OKO	−21.328	−17.127
CO_2, SEW	−21.914	−18.070
CH_4, IFO	−12.807	−7.654
CH_4, JSR	−12.591	−1.442
CH_4, OKO	−16.052	−10.409
CH_4, SEW	−16.404	−12.031

3.4 Binary mixtures

3.4.1 Adsorption isotherms

The adsorption isotherms for equimolar mixtures of CO_2/CH_4 in IFO, JSR, OKO and SEW at 298 K are shown in Fig. 6. With an increase in pressure, the amount of CO_2 adsorbed initially increases linearly and then flattens, while the amount of CH_4 adsorbed changes little. The ratios of equilibrium adsorption capacity for the equimolar mixtures at different pressures are presented in Table 4. It is obvious that with an increase in pressure, the ratio of equilibrium adsorption capacity for CO_2/CH_4 increases. For a pressure swing adsorption (PSA) processes, the adsorption step generally takes place at moderate pressures (5 atm) in view of energy saving. In this condition, the equilibrium adsorption capacities for CO_2 in all zeolites were five times more than those for CH_4, which suggests that the new siliceous zeolites have a strong ability to separate a mixture of CO_2 and CH_4.

3.4.2 Adsorption selectivity

The selectivity coefficient S_{ij} is a good indication of separation ability and is given by the following equation:

$$S_{ij} = (y_i/y_j)/(x_i/x_j) \tag{4}$$

where x_i and x_j are the molar fractions of species i and j in the gas phase, while y_i and y_j are the molar fraction of species i and j adsorbed in the framework, respectively.

The selectivity coefficients of CO_2/CH_4 in the four new zeolites as a function of the partial pressure of CO_2 at a total pressure 1000 kPa are shown in Fig. 7. The results demonstrate that the selectivity coefficients increase with a decrease in the concentration of CH_4 in the mixture. The higher selectivity coefficients for CO_2/CH_4 at a low concentration of CH_4 (<30 mol%) (Zhong et al. 2013) belong to the JSR zeolite. Thus, considering the adsorption uptake and selectivity of CO_2/CH_4, the JSR zeolite is a good candidate for the separation of CO_2/CH_4 at low pressure (up to 1000 kPa).

4 Conclusions

The GCMC method was employed to investigate the adsorption and separation properties for CO_2 and CH_4 in new siliceous zeolites of IFO, JSR, OKO and SEW. The adsorption isotherms for the pure components and binary mixtures of CO_2 and CH_4 in these zeolites were obtained. Adsorption thermodynamic parameters were also analyzed.

The adsorbed amount of pure components increases with an increase in pressure and the adsorption amount for

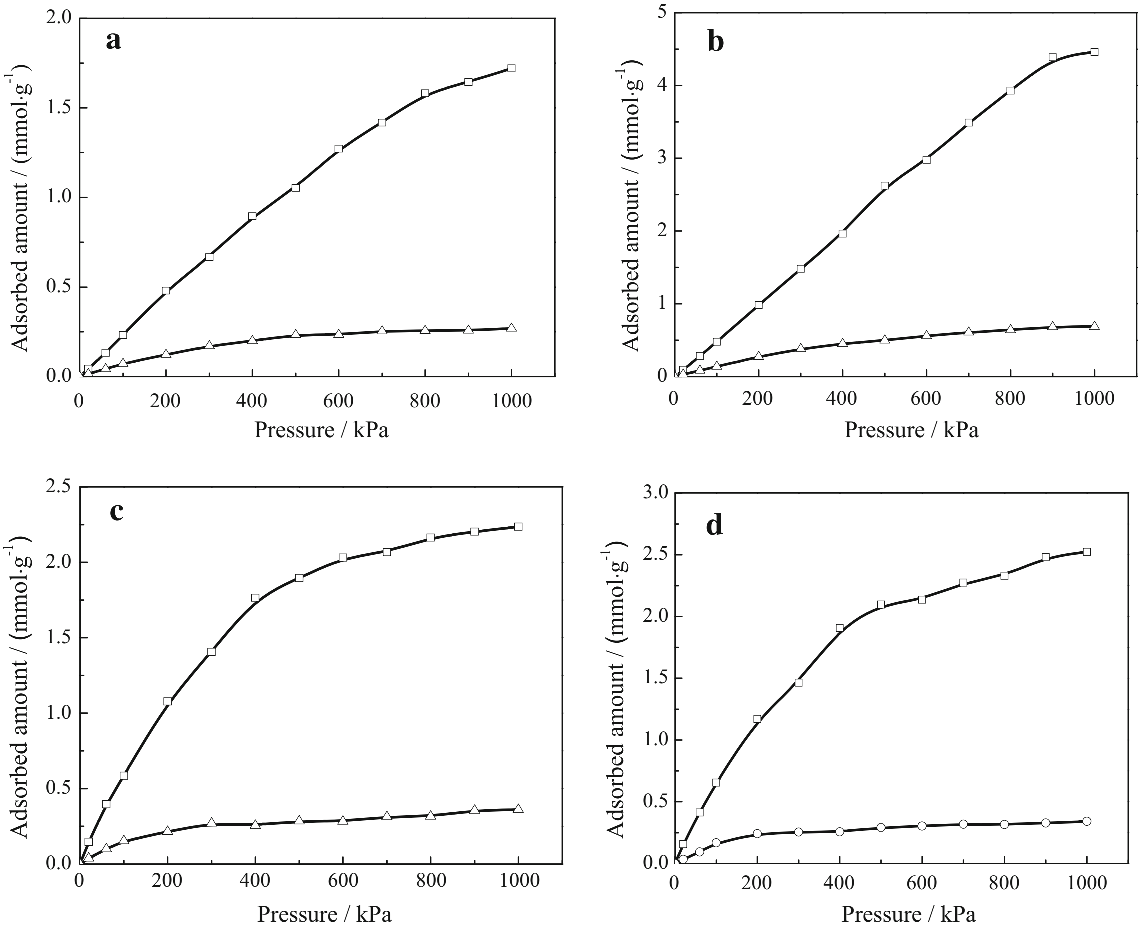


Fig. 6 The adsorption isotherms of the equimolar mixtures of CO_2 and CH_4 in new siliceous zeolites at 298 K: (a) IFO, (b) JSR, (c) OKO, (d) SEW; *open square* CO_2; *open triangle* CH_4

Table 4 The ratios of equilibrium adsorption capacity of CO_2 and CH_4 at different pressures

Zeolites	Pressure (kPa)			
	200	400	600	800
IFO	3.91	4.50	5.43	6.18
JSR	3.60	4.37	5.29	6.13
OKO	5.04	6.91	7.19	6.87
SEW	4.85	7.44	7.03	7.39

both CO_2 and CH_4 in these zeolites can be ranked as follows: JSR > SEW > OKO > IFO. The adsorption amount of CO_2 and CH_4 in the JSR zeolite is 7.08 and 2.27 mmol g^{-1} at 1000 kPa, respectively. The thermo dynamic parameters of Gibb's free energy change and enthalpy change of adsorption show that CO_2 displays a higher affinity than that of CH_4 in the new siliceous zeolites. A negative adsorption entropy change ΔS^0 indicates the CO_2 and CH_4 adsorbed are in an ordered arrangement in all the new zeolites. The more negative entropy for CO_2 when compared with CH_4 in each new zeolite presents a more orderly arrangement of CO_2.

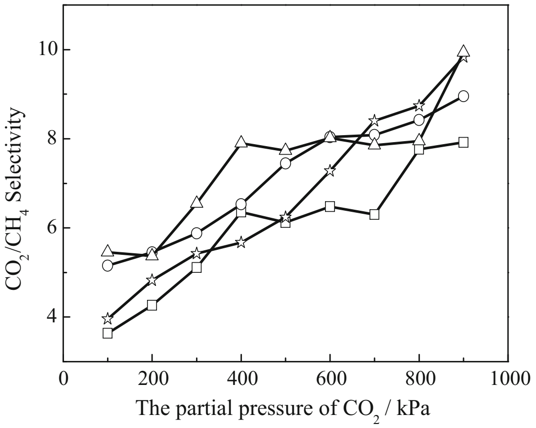


Fig. 7 The selectivity coefficients of CO_2/CH_4 in new siliceous zeolites: *open square* IFO; *open star* JSR; *open circle* OKO; *triangle* SEW

The adsorption isotherms for the binary mixtures suggest the new siliceous zeolites can be used to separate a

CO_2/CH_4 mixture. Considering the adsorption uptake and selectivity for CO_2/CH_4, the JSR zeolite is a good candidate for the separation of CO_2/CH_4 at low pressure (up to 1000 kPa).

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