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Adsorption of CO_2 and N_2 on synthesized NaY zeolite at high temperatures

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Abstract NaY zeolite particles with a high surface area of 723 m^2/g were synthesized by a hydrothermal method. Adsorption isotherms of pure gases CO_2 and N_2 on the synthesized NaY particles were measured at temperatures 303, 323, 348, 373, 398, 423, 448 and 473 K and pressures up to 100 kPa. It was found that the adsorption isotherm of CO_2 on the synthesized zeolite is higher than that on other porous media reported in the literature. All measured adsorption isotherms of CO_2 and N_2 were fitted to adsorption models Sips, Toth, and UNILAN in the measured temperature/pressure range and Henry's law adsorption equilibrium constants were obtained for all three adsorption models. The adsorption isotherms measured in this work suggest that the NaY zeolite may be capable of capturing CO_2 from flue gas at high temperatures. In addition, isosteric heats of adsorption were calculated from these adsorption isotherms. It was found that temperature has little effect on N_2 adsorption, while it presents marked decrease for CO_2 with an increase of adsorbate loading, which suggests heterogeneous interactions between CO_2 and the zeolite cavity.

Keywords Adsorption isotherm · Isosteric heat of adsorption · Zeolite · CO_2 capture

Nomenclature

b	Parameters for Sips model, kPa^{-1}
c	Parameters for UNILAN model, kPa
DQ	Standard deviation, %
k	Number of experimental data
K	Parameters for Toth model, kPa^{-1}
m	Parameters for Toth model
n	The magnitudes of moles adsorbed, mol/kg
n^{cal}	Adsorbed values calculated from models, mol/kg
n^{exp}	Adsorbed values from experiment, mol/kg
n_s	Parameter for adsorption models, mol/kg
N	Adsorbate loading, mol/kg
P	Pressure at equilibrium state, kPa
q	Parameters for Sips model
Q_{st}	Isosteric heat of adsorption, J/mol
R	Gas constant, 8.314, J/mol/K
s	Parameter for UNILAN model
T	Temperature, K
Δn	Average percentage of deviation, %

1 Introduction

Fossil fuels as the world-wide applied resource fulfill more than 90% of the world's energy needs (Birol and Argiri 1999). Correspondingly, the combustion of fossil fuels is one of the major causes of the greenhouse gas carbon dioxide (CO_2), which is considered to take the major responsibility to the existence of global warming effect (Epstein and Rogers 2004). In order to reduce the excessive CO_2 emission, among many developed methods, separation and adsorption are believed to play a promising role in carbon capture from flue gases (Reichle et al. 1999). Gas adsorption with microporous materials has attracted much attention due to its great practical importance in the fields of gas separation, gas purification, and environmental problems.

It is important to select the proper adsorbent for the design of an efficient adsorption process. Due to the requirements for the adsorbents, such as the high selectivity and adsorption capacity for CO_2, stable adsorption ca-

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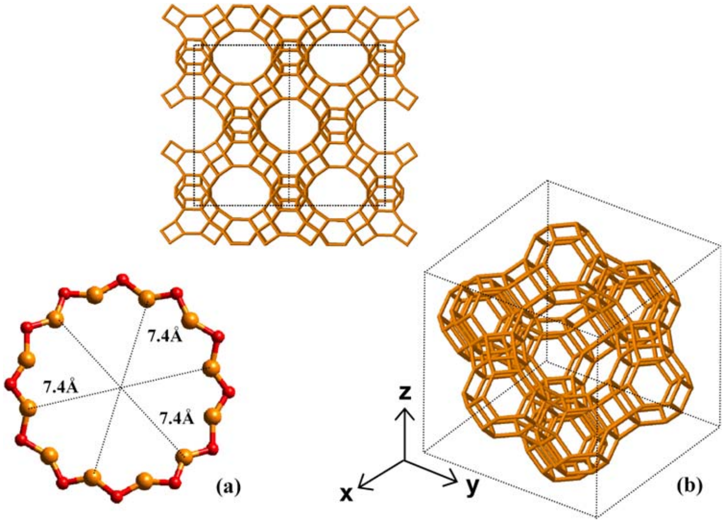

Fig. 1 Framework of NaY zeolite and the supercage of 12-member ring (**a**) viewed along [111] (**b**). *Top middle*: projection down [110] (Meier and Olson 2001)

pacity after repeated adsorption cycles, and adequate adsorption/desorption kinetics and mechanical strength of the adsorbents after cyclic exposure to high-pressure streams, many efforts have made to develop and evaluate a wide range of porous adsorbents including carbon-based adsorbents, metal oxide sorbents, hydrotalcite-like compounds, CaO-based sorbents, zeolites, etc. (Yong et al. 2002; Florin and Harris 2008). Amines, particularly aqueous monoethanolamine (MEA), are the first generation of CO_2 post-combustion capture because amine absorption is reliable, efficient and reasonable cost for processing a large amount of CO_2. There are a number of investigations on amine absorption processes for industrial applications (Adams and Davison 2007; Liu et al. 1999). As unique solid adsorbents, however, zeolites are highly effective for removing the relatively minor amount of CO_2 that are present in a large gas flow (Abanades et al. 2004).

Zeolites comprising variable sizes of sieves and pores are widely used for gas separation and purification, ion exchange, and catalytic processes. These crystalline aluminosilicates have relatively rigid three-dimensional structures formed by TO_4 tetrahedra ($T = Si$ and Al) (Meier and Olson 2001). Every T-atom is connected by oxygen to four other T-atoms to create pores and channels. Exchangeable cations within the cavities are located to balance the negative charge introduced onto the framework by the aluminum atoms. Since zeolites have well-defined pores and channels, they are often used as adsorbents for different purposes according to their various chemical properties and channel geometry. NaY zeolite in particular has a wide range of commercial uses due to its stable crystal structures and three-dimensional large pores. NaY zeolite has identical 7.4 angstroms supercage structures as described in Fig. 1 (Meier and Olson 2001), which is composed by 12 members of T-atoms.

The relevant adsorption equilibrium is, theoretically, an essential requirement for the analysis and design of adsorption separation processes. For the practical applications, the adsorption equilibrium must be available over a broad range of operation temperatures and pressures. Regarding CO_2 adsorption and separation, it is of great significance to obtain high CO_2 adsorption capacity because the CO_2 adsorption behavior greatly influences the CO_2 separation and desorption processes on NaY particle and membrane. A number of efforts have been made to address CO_2 adsorption behavior via different adsorbents and techniques (Lee et al. 2002; Harlick and Tezel 2004; Li and Tezel 2007; Siriwardane et al. 2003; Jaramillo and Chandross 2004; Khelifa et al. 2004; Li et al. 2000, 2008; Walton et al. 2006; Maurin et al. 2005; Gao et al. 2004; Kusakabe et al. 1997, Plant et al. 2006, 2007; Sebastian et al. 2007; Chou and Chen 2004; Othman et al. 2006; Zheng and Gu 1998). Yong et al. (2002) reviewed the adsorption of CO_2 on different adsorbents at relatively high temperatures. Those adsorbent materials included carbon-based adsorbent, metal oxide sorbents, zeolite and hydrotalcite-like compounds (HTlcs). They concluded that only HTlcs and basic alumina have favorable adsorption ability of CO_2. Nevertheless, they only selected data of zeolite ASRT 5A to compare with other adsorbents, which wasn't sufficient at all, taking into account that there are hundreds of types of zeolites. Moreover, as an adsorbent, the application of HTlcs was greatly limited by their rather low CO_2 adsorption at room temperature. For instance, with increasing temperature, the quantity of adsorbed CO_2 was observably decreased. But surprisingly, when the temperature reached 573 K, the amounts of adsorbed CO_2 increased sharply. Through a measured series of CO_2 adsorption experiments on a large amount of adsorbents, including NaY, NaX, ZSM-5, 5A and 13X, Harlick and Tezel (2004) persuasively drew a conclusion that, among wide choices of adsorbents, zeolite 13X and Y were shown to be the most

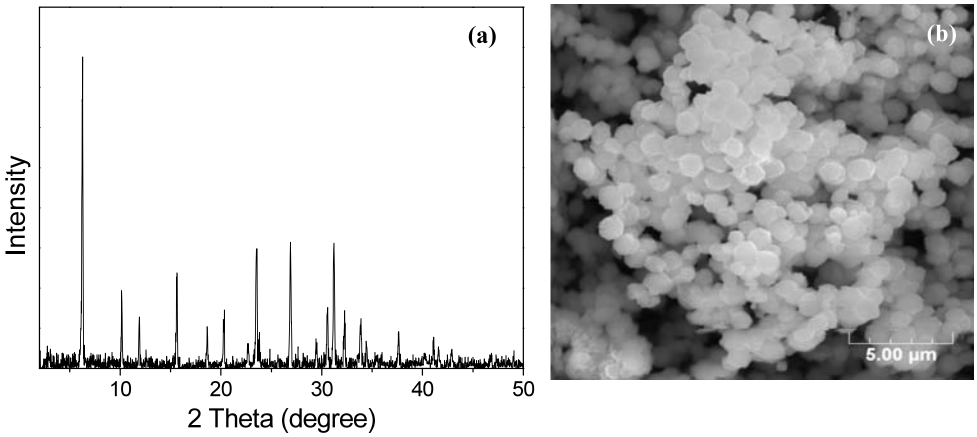

Fig. 2 (**a**) X-ray diffraction pattern and (**b**) SEM image of the synthesized NaY zeolite particles

suitable CO_2 adsorbents for given conditions corresponding to low-pressure CO_2 feed and regeneration. However, the adsorption data of CO_2 on other adsorbents, such as natural zeolites, β-zeolite, were not available in their paper. Li and Tezel (2007) also compared the dimensional Henry's Law adsorption equilibrium constants of CO_2 on β-zeolite and NaY zeolite and came to a similar conclusion that the NaY zeolite has better CO_2 adsorption capacity. Siriwardane et al. (2003) and Jaramillo and Chandross (2004) studied CO_2 adsorption behavior on natural zeolites and zeolite 4A, but it was found that the amounts of CO_2 adsorption on natural zeolite and zeolite 4A were lower than that on the NaY zeolite reported by Harlick and Tezel (2004). Thus, adsorption isotherms of pure gas (e.g., CO_2) on the NaY zeolite, particularly at high temperature, are needed to study carbon capture from flue gas.

In this work, we synthesized the NaY zeolite particles with high surface areas and measured adsorption isotherms of single gases CO_2 and N_2 on the NaY zeolite at temperatures from 303 K to 473 K and pressures up to 100 kPa. A comparison of the quantities of CO_2 adsorption isotherms measured in the present work with other results available in the literatures was made afterwards. The measured adsorption isotherms were then correlated to adsorption models Sip, Toth and UNILAN, which are widely utilized for modeling microporous materials adsorption. The isosteric heats of adsorption were also calculated from these adsorption isotherms.

2 Experimental

2.1 Materials

The NaY zeolite particles were synthesized from an aluminosilicate gel with a molar composition of SiO_2:Al_2O_3:Na_2O:H_2O = 12.8:1:17:675. The synthesis gel was prepared by mixing sodium hydroxide (99.99%, Sigma-Aldrich), sodium aluminate (50∼56% Al, 40∼45% Na, Fe < 0.05, Riedel-de Haën], and sodium silicate solution (27% SiO_2, 14% NaOH, Sigma-Aldrich) in distilled water at ambient temperature. The resulting gel solution was continuously stirred and aged for 24 hours. The hydrothermal synthesis of NaY particles was prepared at 363 K for 12 hours. The synthesized zeolite was centrifuged and washed by distilled water until the pH value reached 7∼8, then the obtained particles were dried at 383 K overnight.

2.2 Apparatus

The characterizations of the crystal structure and morphology of NaY particles were conducted by X-ray diffraction (Siemens D500) and field emission scanning electron microscope (Hitachi S-800). The adsorption isotherms of CO_2 and N_2 on the NaY zeolite particles were measured by the accelerated surface area and porosimetry analyzer system ASAP 2020 (Micromeritics).

Prior to each isotherm adsorption measurement, a combined vacuum system of a mechanical vacuum pump and an ionization pump provided a vacuum as low as 3 μm Hg. To eliminate the influence of impure gases, the sample tube was heated to 623 K at a heating rate of 10 K/m then held for a couple of hours. Meanwhile, the volumes of the manifold and sample tube were backfilled by expansion of helium gas and re-degassed for a few times. Then, the desired amount of CO_2 or N_2 was supplied to the manifold and sample tube with auto-controlled valves.

3 Results and discussions

Figure 2 shows the X-ray diffraction pattern and SEM image of the synthesized NaY particles. It is found that the synthesized NaY particles with uniform particle size of about 1 μm have a good agreement with the standard NaY X-ray diffraction pattern.

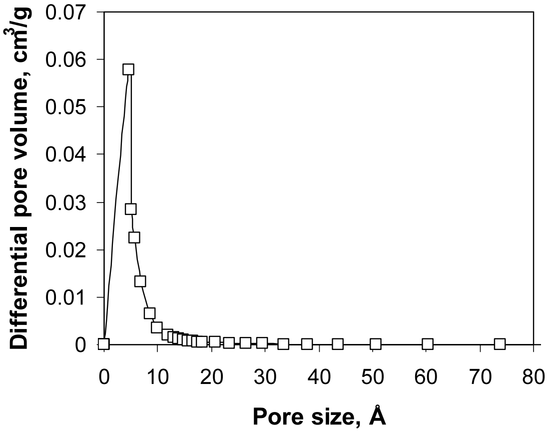

Fig. 3 Pore size distribution of the synthesized NaY zeolite by BET measurements

The surface area, micropore volume and pore diameter of the NaY zeolite were measured by the ASAP 2020 system using nitrogen adsorption at 77.3 K. The synthesized NaY zeolite has BET surface area 723 m^2/g, micropore area 677 m^2/g and micropore volume 0.35 cm^3/g. The pore size distribution plot is presented in Fig. 3. It shows a unique pore size distribution of the synthesized NaY zeolite particles.

Adsorption isotherms for single gases CO_2 and N_2 on the synthesized NaY zeolite particles were measured at temperatures 303, 323, 348, 373, 398, 423, 448 and 473 K and pressures up to 100 kPa. Figures 4a and 4b present adsorption isotherms of CO_2 and N_2 on synthesized NaY particles at different temperatures and pressures, respectively. The amount of CO_2 adsorbed on the NaY zeolite was remarkably larger than that of N_2 within the experimental range of temperature and pressure. For example, the quantities of adsorbed CO_2 and N_2 are 4.8 mol/kg and 0.33 mol/kg at 303 K and 100 kPa, respectively. Moreover, when the adsorption temperature is increased, the adsorbed CO_2 and N_2 on the NaY particles are found to decrease. Figure 5 compares the adsorption isotherms of CO_2 and N_2 on the synthesized NaY at 303 K and 473 K. Obviously, the quantity of adsorbed gas molecules, particularly for CO_2, at 473 K is much lower than those adsorbed at 303 K.

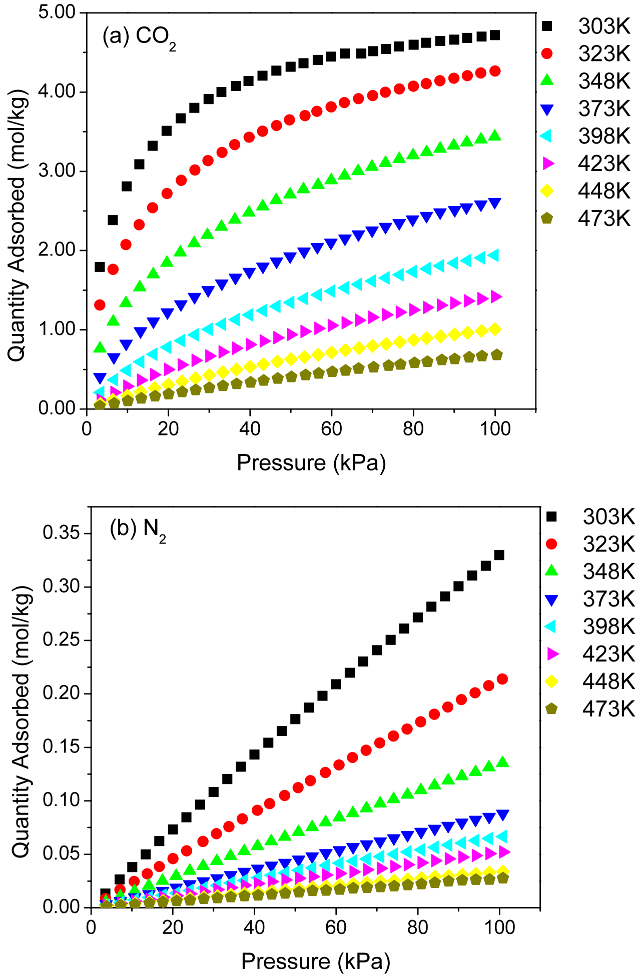

Fig. 4 Experimental adsorption isotherms of (**a**) CO_2 and (**b**) N_2 on the synthesized NaY zeolite at temperatures 303, 323, 348, 373, 398, 423, 448 and 473 K and pressures up to 100 kPa

The molar ratios (CO_2/N_2) of adsorbed single gases on the synthetic NaY zeolite are shown in Fig. 6. The smooth lines fitted to the Toth model (see below) are also plotted in this figure. The larger the molar ratio is, the more CO_2 is adsorbed on the NaY zeolite. At the same temperature, the molar ratio CO_2/N_2 decreases when the pressure increases. For example, at 348 K, the molar ratio of CO_2/N_2 declined from 105 at 6.67 kPa to 26 at 100 kPa. At low pressures (<46.7 kPa), the molar ratio of CO_2/N_2 declines as the temperature increases. Whereas, at higher pressures (>46.7 kPa), the CO_2/N_2 molar ratio tends to increase until it reaches a relatively flat zone with regard to the temperature increase. Within the whole experimental temperatures and pressures, the lowest molar ratio achieved is 15 at 303 K and 100 kPa. In other words, because of the CO_2 preferential adsorption, it will potentially perform a good permselectivity of CO_2/N_2 mixture gases on the NaY zeolite particles or membranes, which could be used for carbon capture from flue gas.

There are quite a few adsorption isotherms for CO_2 adsorption on various porous media available in literature. For example, Harlick and Tezel (2004), Li and Tezel (2007) measured CO_2 adsorption isotherms on a variety of zeolites, including β, 5A, 13X, NaY, H-Y, and H-ZSM at temperatures lower than 373 K. Siriwardane et al. (2003) mainly focused on natural zeolites using pressure swing adsorption technology. Walton et al. (2006) and Maurin et al. (2005) also studied CO_2 adsorption isotherms on zeolites NaX and NaY. In order to compare the CO_2 adsorption capacity in this work with others, we plot the CO_2 adsorption isotherms at near room temperature (303 K) and pressures up to 100 kPa available in the literature and the measurement

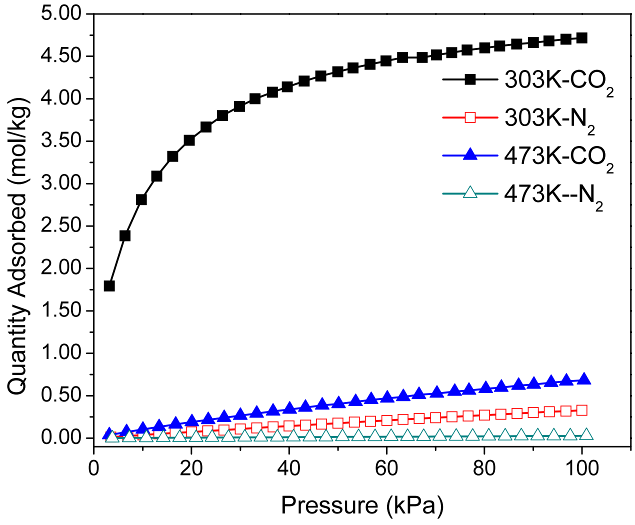

Fig. 5 A comparison of adsorption isotherm of CO_2 and N_2 on the synthesized NaY zeolite at 303 K and 473 K

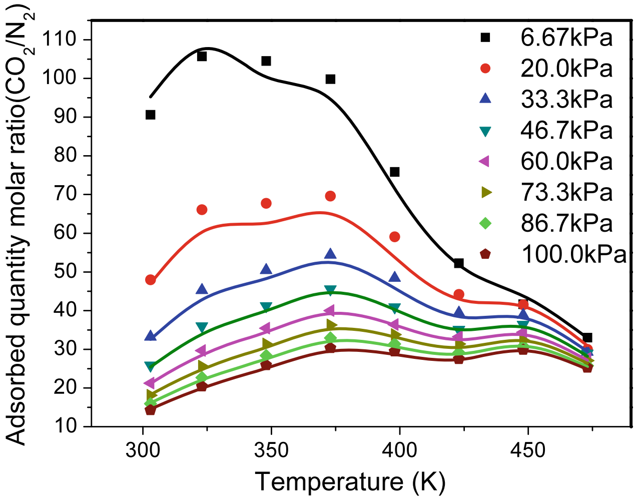

Fig. 6 Molar ratio of CO_2/N_2 adsorbed on the synthesized NaY zeolite at different pressures in the range of temperatures from 303 K to 473 K. Much more adsorbed CO_2 is observed at the same temperature and pressure. *Symbols* are plotted from measurement; *lines* are smoothed from Toth model fitting

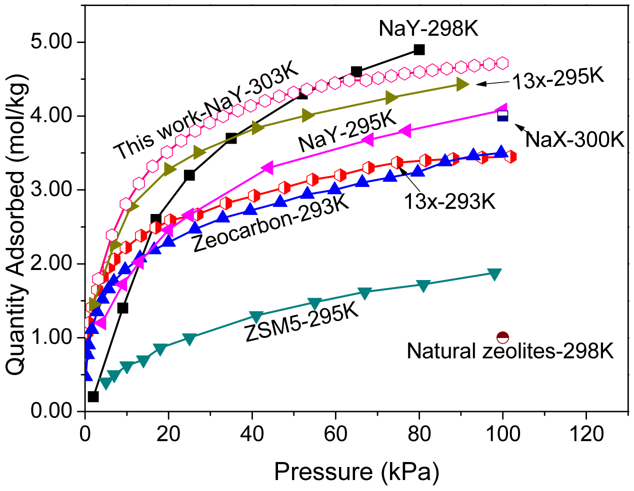

Fig. 7 Adsorption isotherms of CO_2 on the synthesized NaY-303 K (this work), NaY-298 K (Walton et al. 2006), 13X-295 K (Harlick and Tezel 2004), NaY-295 K (Harlick and Tezel 2004), NaX-300 K (Maurin et al. 2005), 13X-293 K (Lee et al. 2002), zeocarbon-293 K (Lee et al. 2002), ZSM5-295 K (Harlick and Tezel 2004), and natural zeolites-298 K (Siriwardane et al. 2003). *Lines* are for guiding the eyes

in this work, as shown in Fig. 7. It is found that, compared with other adsorbents including NaX, 13X, ZSM-5, Zeocarbon, and natural zeolites, the CO_2 adsorption isotherms in this work and the one by Walton et al. (2006) produce better quantities on the NaY zeolites. At a pressure about 80 kPa, the adsorbed CO_2 is 4.6 mol/kg at 303 K on the synthesized NaY particles in this work and about 4.9 mol/kg at 298 K on those by Walton et al. (2006). It is slightly higher than the value in this work, however, the adsorption of CO_2 measured in this work is apparently higher than that the one obtained by Walton et al. (2006) at the pressures below 50 kPa. Moreover, the adsorption temperature used in this study was 303 K, while it was 298 K in those measurements by Walton et al. (2006). Therefore, it is reasonable to extrapolate that the actual adsorption of CO_2 at 298 K on the NaY zeolite synthesized in this work could be close to or even higher than that obtained by Walton et al. (2006). In other words, it is safe to conclude that comparing the adsorption isotherms available in the literature, the synthesized NaY zeolite particles in this work performs better CO_2 adsorption behavior.

It should be mentioned that the presence of moisture affects the adsorption of CO_2 on the NaY zeolite because the zeolitic pores are blocked primarily by H_2O molecules (Gu et al. 2005). In this study we measured adsorption isotherms of CO_2 and N_2 on the synthetic NaY zeolite, but we have been synthesizing the NaY membranes for CO_2 capture from a simulated flue gas (CO_2, N_2, H_2O, H_2S, etc). Studies on the effect of moisture on CO_2/N_2 adsorption and separation are in progress.

The adsorption isotherm can be generally expressed by these models: Sips (Paul and Clyde 1997), Toth (Toth 1984) and UNILAN (Hill 1949; Do 1998), which are given in (1), (2), and (3) respectively.

$$n = \frac{n_s b P^{1/q}}{1 + b P^{1/q}} \tag{1}$$

$$n = \frac{n_s K P}{[1 + (K P)^m]^{1/m}} \tag{2}$$

$$n = \frac{n_s}{2s} \ln\left(\frac{c + P e^{+s}}{c + P e^{-s}}\right) \tag{3}$$

Sips model (1) assumes the surface of adsorbent is heterogeneous and is similar to the Freundlich equation (Freundlich 1921), which is generally applied at relatively high

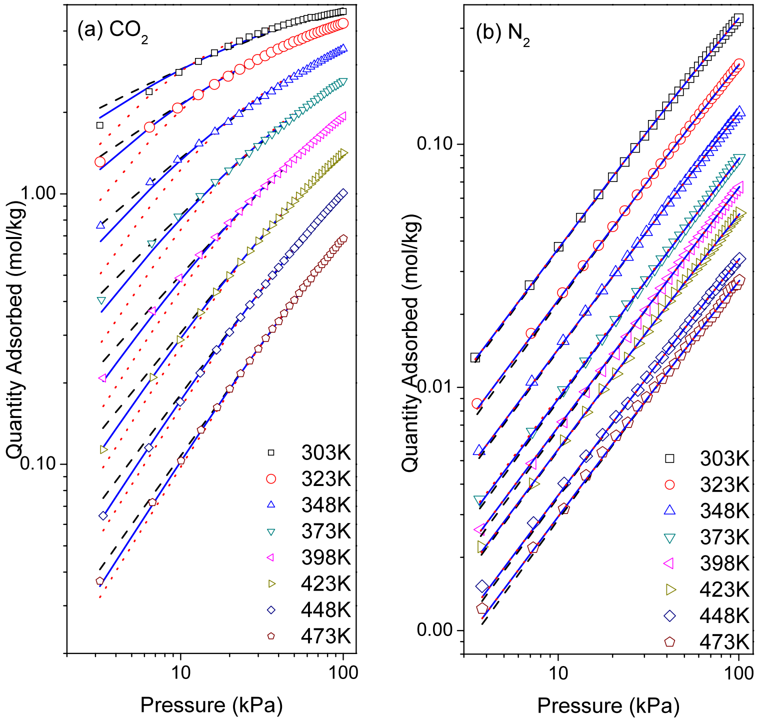

Fig. 8 Logarithmic correlation of adsorption isotherms of (**a**) CO_2 and (**b**) N_2 on the synthesized NaY zeolite at temperatures from 303 K to 473 K and pressures up to 100 kPa by using models Sips (*dash lines*), Toth (*solid lines*) and UNILAN (*dot lines*)

pressure, except a finite limit if the pressure is sufficiently high. The Toth model (2) is appropriately used to describe many systems with submonolayer coverage because of its simple formula and acceptable correctness. UNILAN mode (3) presuming the distribution of energy on the adsorbent surface is uniform is an empirical equation derived from the assumption that the surface of the adsorbent is comprised of ideal continuous patches which are eligible for the Langmuir isotherm.

We fitted all the measured adsorption isotherms of pure gases CO_2 and N_2 to these three models. The fitted adsorption isotherms are presented in Fig. 8. All the fitted data for the three models are good except for those at lower pressures. To further represent the fitting, we calculated the standard deviations of adsorbed CO_2 and N_2, $DQ\%$, defined as

$$DQ/\% = 100\left[\frac{n_j^{\text{exp}} - n_j^{\text{cal}}}{n_j^{\text{exp}}}\right] \tag{4}$$

The calculated DQ% shows that standard deviations at low pressures (<10 kPa) (average: 10%) are larger than those at high pressures (average: 2%) and that all fittings become much better for the three models in high pressure region.

Table 1 lists all fitted parameters n_s, b, q for Sips model, n_s, K, m for Toth model and n_s, c and s for UNILAN model. n_s and c, K, b are related to the monolayer capacity and Henry's law slope; s, m and q are numerical isotherm parameters. Δn in Table 1 stands for the average percent deviations for fitted adsorption isotherms, defined by

$$\Delta n/\% = \frac{100}{k}\sum_{j=1}^{k}\left|\frac{n_j^{\text{exp}} - n_j^{\text{cal}}}{n_j^{\text{exp}}}\right| \tag{5}$$

Table 1 suggests that applying Sips and Toth models results in a much better fitting for CO_2 adsorption than UNILAN. However, the performances of all the three models fitting for N_2 adsorption are comparable with each other. Overall, the Toth model provides better fitting data than Sips and UNILAN models under the entire experimental temperature range. Since the adsorption isotherm at different temperatures (adsorption equilibrium constants) follows the Henry's law, we plot the slopes for each model for the adsorption of CO_2 and N_2 in Figs. 9a and 9b, respectively. A good linear relationship is observed for the parameters n_s vs. the reciprocal of the adsorption temperature. The correlation coefficients of linear fitting to models Sips, Toth and UNILAN are 1.000, 1.000 and 1.000 for CO_2 and are 0.980, 0.984 and 0.975 for N_2, respectively.

The isosteric heat of adsorption, a critical design variable in estimating the performance of an adsorptive gas separation process, is used to measure the interaction between adsorbate and adsorbent molecules as well as the energetic heterogeneity of the adsorbent surface. In general, if the adsorbent is homogeneous, it would exhibit a constant value with increasing adsorbate loading. If it decreases with increasing adsorbate uptake, the energetic heterogeneity of the

Table 1 Fitted parameters for adsorption models Sips, Toth, and UNILAN

	Sips							
	CO$_2$				N$_2$			
T (K)	n_s	b	q	Δn %	n_s	b	q	Δn %
303	8.97	0.190	2.52	2.50	2.20	0.00165	0.986	0.512
323	8.33	0.111	2.03	0.978	1.61	0.00132	0.971	0.976
348	7.61	0.0569	1.72	0.147	1.28	0.00108	0.984	0.627
373	7.02	0.0304	1.55	0.476	1.01	0.000831	0.973	0.918
398	6.46	0.0164	1.41	0.983	0.810	0.000791	0.974	0.952
423	5.97	0.00928	1.31	1.72	0.453	0.00121	0.986	1.13
448	5.64	0.00501	1.22	1.67	0.295	0.00115	0.980	1.30
473	5.25	0.00290	1.17	1.25	0.220	0.00124	0.972	2.31

	Toth							
	CO$_2$				N$_2$			
T (K)	n_s	K	m	Δn %	n_s	K	m	Δn %
303	7.39	0.817	0.388	1.50	2.81	0.00135	0.966	0.320
323	7.11	0.214	0.446	0.500	2.40	0.000965	1.02	0.407
348	6.79	0.0701	0.479	1.41	1.91	0.000763	0.968	0.348
373	6.55	0.0297	0.496	1.49	1.25	0.000722	1.18	0.481
398	6.32	0.0136	0.505	0.831	0.986	0.000704	1.13	1.17
423	6.13	0.00710	0.539	0.150	0.758	0.000749	0.911	1.03
448	5.93	0.00371	0.574	0.201	0.502	0.000730	0.947	0.966
473	5.76	0.00210	0.588	0.471	0.381	0.000787	0.949	1.73

	UNILAN							
	CO$_2$				N$_2$			
T (K)	n_s	c	s	Δn %	n_s	c	s	Δn %
303	7.89	7.693	0.800	1.38	2.31	1230	1.25	0.325
323	7.48	13.76	0.799	2.89	2.25	2092	1.29	0.391
348	7.01	25.55	0.777	3.92	1.49	2309	1.31	0.353
373	6.61	42.09	0.745	3.98	1.28	2639	1.23	0.676
398	6.30	66.08	0.710	3.19	1.03	4840	1.51	1.21
423	5.97	99.10	0.684	2.00	0.550	1857	1.23	1.05
448	5.71	155.5	0.665	1.54	0.365	2259	1.31	0.982
473	5.47	227.1	0.632	1.50	0.209	2957	1.66	1.74

adsorbent surface is revealed; while the heat increases with increasing adsorbate loading, it is due to the stronger lateral interactions between adsorbed molecules at higher surface coverage. The theoretical and experimental studies on the isosteric heat of adsorption have been carried out on a number of adsorbates on various microporous and mesoporous adsorbents including zeolites (Khelifa et al. 2004; Dunne et al. 1996, Chakraborty et al. 2006, 2008, Sircar et al. 1999; Sircar 2005). All three trends of the heat were observed for those adsorbate-adsorbent systems.

The isosteric heats of adsorption, Q_{st}, at specific adsorption loading of the measured single gases CO$_2$ and N$_2$ were calculated in this work by the Clausius-Clapeyron equation

$$Q_{st} = RT^2\left(\frac{\partial \ln P}{\partial T}\right)_N \qquad (6)$$

If Q_{st} is temperature independent for a given amount of gas adsorbed, the plot of $\ln P$ against $1/T$ should reveal straight line.

The isosteric heat of adsorption as a function of adsorbed CO$_2$ (filled squares) and N$_2$ (opened circles) on the synthe-

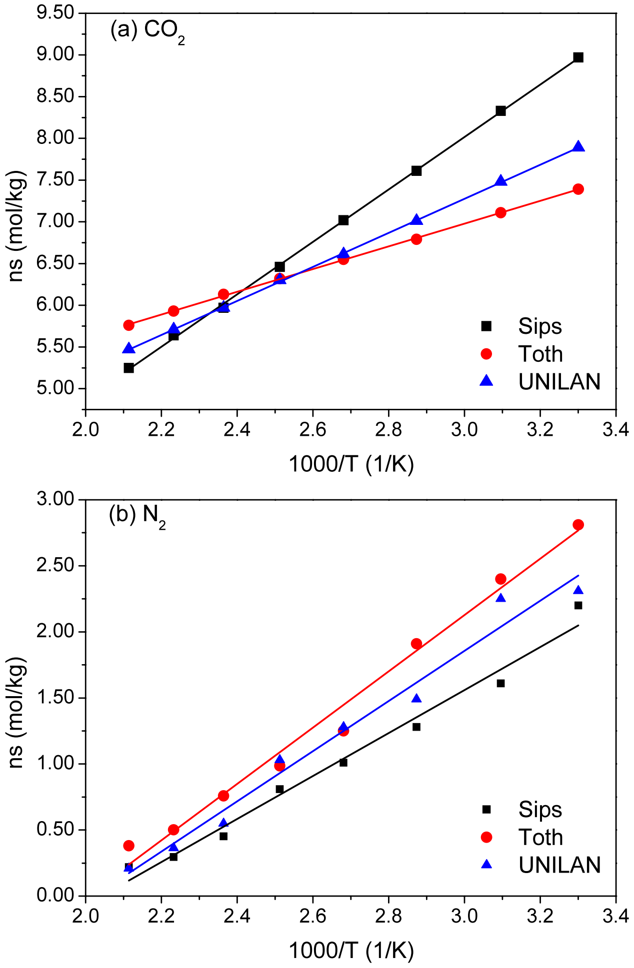

Fig. 9 Plot of parameters n_s fitted to models Sips (*squares*), Toth (*circles*) and UNILAN (*triangles*) for adsorption isotherms of (**a**) CO_2 and (**b**) N_2 on the synthesized NaY zeolite. The correlation coefficients of linear fitting to models Sips, Toth and UNILAN are 1.000, 1.000 and 1.000 for CO_2 are 0.980, 0.984 and 0.975 for N_2, respectively

sized NaY zeolite is shown in Fig. 10. The isosteric heat of adsorption for N_2 on the NaY has little change (average is about 18 kJ/mol), indicating that the interaction between the weak quadrupole moment of N_2 and the NaY does not introduce significant heterogeneity for N_2 adsorption. On the contrast, the isosteric heat of adsorption for CO_2 presents a decrease from 40 to 12 kJ/mol. The decrease of the heat with coverage is attributed to interactions of Na^+ ions with the quadrupole moment of CO_2, which suggests strong interactions between the large quadrupole moment of CO_2 and the adsorbent NaY zeolite. The same trend of the heat changing with CO_2 loading has been found by others (Dunne et al. 1996; Sircar et al. 1999; Sircar 2005). Khelifa et al. (2004) found a continuous decrease in the isosteric heat of adsorption with introduction of Cr^{3+} to NaX zeolites, which could ascribed to a progressive weakening of electrostatic fields present within zeolite cavities. It suggests that the interaction between CO_2 and the zeolite surface have a progressive decrease with CO_2 loading. The adsorption of CO_2 on the NaY in this work has a similar weakening interaction between CO_2 and the zeolite cavity with CO_2 loading, which could result in a decrease in the isosteric heat of adsorption.

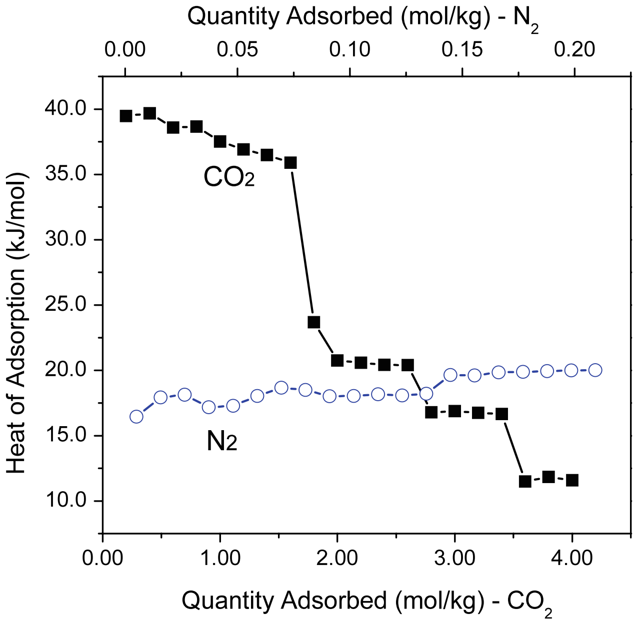

Fig. 10 Isosteric heats of adsorption for CO_2 (*filled squares*) and N_2 (*opened circles*) on the synthesized NaY zeolite particles. *Lines* are for guiding the eyes

4 Conclusions

The NaY zeolite particles with a high surface area of 723 m^2/g were synthesized by a hydrothermal method. Adsorption isotherms of pure gases CO_2 and N_2 on the synthesized NaY particles were measured at temperatures 303, 323, 348, 373, 398, 423, 448 and 473 K and pressures up to 100 kPa. All adsorption data were correlated to adsorption models Sips, Toth, and UNILAND. Generally, the amount of adsorbed CO_2 is much larger than that of adsorbed N_2 and high molar ratios (CO_2/N_2) are observed in the range of measured temperatures and pressures. Compared to CO_2 adsorption isotherms on various zeolites available in the literature, the synthesized NaY zeolite particles in this work shows the better CO_2 adsorption behavior. A good correlation of measured adsorption isotherms of CO_2 and N_2 on the NaY zeolite to Sips, Toth, and UNILAN models is found and linear relationships are observed for the parameter n_s vs. reciprocal of temperature for the three models. The calculated isosteric heats of adsorption from these adsorption isotherms show that temperature has little effect on N_2 adsorption, while they present marked decrease for CO_2 with an increase of adsorbate loading, which suggests heterogeneous interactions between CO_2 and the zeolite cavity. The hydrothermally synthesized NaY zeolite in this work demonstrates a better adsorption behavior for CO_2 separation and could be one of good candidates for carbon capture from flue gas.

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