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CO_2 adsorption in LiY and NaY at high temperature: molecular simulations compared to experiments

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Abstract Grand Canonical Monte Carlo simulations combined with adsorption measurements have been carried out to gain further insight into the CO_2 adsorption process at the microscopic scale in both LiY and NaY faujasites at various temperatures. A new Li^+-CO_2 force field derived by *ab initio* calculations was validated by a reasonable agreement between the simulated isotherms and those obtained by experiments in a wide range of temperature (from 323 K to 473 K). In addition, the microscopic mechanisms of CO_2 adsorption in both systems, consistent with the trends observed for the simulated differential enthalpies of adsorption as a function of the loading, were proposed. It was observed that two different types of adsorption behaviour exist for NaY and LiY at 323 K and 373 K, mainly caused by the significant more exposed position of the SII Na^+ from the six-ring plane of the supercage compared to those occupied by the SII Li^+, whereas at higher temperature, both faujasites exhibit the same flat profile for the differential enthalpy of adsorption as a function of loading.

Keywords CO_2 · LiY · NaY · Adsorption mechanism · Isotherm · Enthalpy of adsorption · High temperature · GCMC simulations · Interatomic potentials · Adsorption measurements

1 Introduction

Alkali-exchanged zeolite microporous materials are involved in a large domain of chemical science and technology including catalytic and separation processes (Corma 2003) or gas storage. In the past few years, several experimental studies (Bezus et al. 1971; Dzhigit et al. 1971; Macedonia et al. 2000) have dealt with the influence of either the nature or density of these extra-framework cations on the adsorption properties of various zeolite systems. It was clearly established that these cations play a key role in the adsorption phenomena in such materials. For instance, the lithium and calcium cation exchanged Faujasites are adsorbents (Coe 1992) in the separation of air by pressure/vacuum swing adsorption procedures whereas the barium exchanged form is involved in the selective separation of aromatic molecules (Neuzil 1971). The cation-containing zeolites are also very promising materials for selective adsorption and separation of carbon dioxide (Harlick and Tezel 2004). The NaX faujasites are thus currently involved as adsorbents in Pressure Swing Adsorption (PSA) based system (Ruthven et al. 1994). This technology is known to be one of the most efficient and economical processes to recover carbon dioxide in flue streams from power plants and incinerators and thus solve energy and environmental problems that the society faces today. Since the last few years, our main interest was to better understand the interactions between different gases such as Ar, N_2, CH_4 and CO_2 and a series of faujasites X and Y containing various monovalent (Li^+, Na^+, K^+) and divalent (Ba^{2+}, Ca^{2+}, Mn^{2+}) cations

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(Maurin et al. 2005a, 2005b, 2005c; Llewellyn and Maurin 2005a). It was clearly shown that the combination of microcalorimetry and molecular simulations is a powerful tool for establishing correlations between the microscopic adsorption behaviours in these systems, which are mainly governed by specific interactions between the adsorbates and the field gradient generated by the cations, and the equilibrium thermodynamic properties. Our recent investigation was focused on the CO_2 adsorption in NaX and NaY at ambient temperature by using Grand Canonical Monte Carlo simulations in conjunction with microcalorimetry (Maurin et al. 2005d). This study allowed us to provide a complete description of the adsorption mechanism in a wide range of pressure which mainly involves interactions between the adsorbates and the sodium ions located in different crystallographic positions within the supercage. It was completed by a quantum chemical study based on DFT calculations which predicted the cation-CO_2 geometries and the associated enthalpies in a series of alkali cation exchanged Y-Faujasite (Plant et al. 2006). Here, we propose to investigate the adsorption of CO_2 in both LiY and NaY at high temperature using Grand Canonical Monte Carlo (GCMC) simulations and adsorption measurements, which is particularly interesting for both fundamental and applied research as the industrial PSA process can be operated at high temperatures for the removal and recovery of carbon dioxide from hot fuel gas streams (Gaffney et al. 1999). In such a process, the main issue is to both characterise the adsorption capacity of carbon dioxide and better understand the adsorption-desorption mechanism on different types of materials in these specific experimental conditions, before selecting the appropriate adsorbent (Yong et al. 2002). Although there has been extensive research on the adsorption of carbon dioxide in a wide range of adsorbent materials at ambient temperature and low pressure (Harlick and Tezel 2004), only a limited number of experimental and theoretical studies at higher temperatures have been published so far in the literature. They mainly report adsorption isotherms in different zeolites such as Na-4A (Yucel and Ruthven 1980; Akten et al. 2003; Jaramillo and Chandross 2004), ZSM-5 (Hirotani et al. 1997) and 13X (Lee et al. 2002) for temperature ranging from 273 K to 498 K without providing any insights onto the adsorption mechanism which is expected to be significantly different compared to those observed at ambient temperature. It has to be noticed that the measurements of adsorption isotherms at different temperature are usually performed only for estimating the adsorption enthalpy by using isosteric methods (Llewellyn and Maurin 2005a).

Here, NaY and LiY are selected as model adsorbents for better understanding the influence of the extra-framework cations on both the adsorption capacity and the microscopic mechanism in a wide range of temperatures [323–473 K]. As the literature did not provide accurate and robust force-fields for describing the interactions between CO_2 and Li^+ cation, our initial step consisted of deriving a self consistent set of potential parameters by using our recently *ab initio* clusters approach we successfully used for representing the Na^+-CO_2 interaction (Plant et al. 2007). From these interatomic potentials, the adsorption properties of the two faujasite systems evaluated by GCMC simulations are reported including both the differential enthalpies and isotherms of adsorption in a wide range of temperature [323–473 K] up to 12 bars. The simulated adsorption isotherms are then compared and contrasted with those measured experimentally in order to test the validity of the derived force fields and their transferability to accurately investigate the high temperature domain. Once, we get a reasonable agreement with the experimental data, the following step consists of exploring the preferential adsorption sites and emphasizing the influence of both the nature of the extra-framework cation and the temperature on the microscopic mechanisms for CO_2 adsorption in both faujasite systems consistent with the corresponding evolution of the differential enthalpy of adsorption as a function of the coverage.

2 Experimental

2.1 Materials

The NaY faujasite in powder form was kindly provided by Zeolyst, and was used as a parent sample to prepare LiY by ion exchange. Four consecutive exchange steps were performed with a 1 molar solution of LiCl (20 g of solid immersed in 200 mL of solution), each for 4 h under constant agitation at 353 K. After each exchange, the samples were filtered, washed with distilled water, dried and finally activated under nitrogen flow up to 623 K at 1 K·min^{-1}. The final degree of exchange was 73%.

The Table 1 reports the textural and chemical analysis of the two samples.

Table 1 Textural characteristics and chemical analysis of LiY and NaY faujasites

Sample	% Si	% Al	% Na	% Li	Si/Al	$S_{BET}/m^2/g$	DubV cm^3/g	Weight loss % (LHPG activation)
NaY	21.4	8.7	6.6	*	2.54	715	0.298	33.8
LiY	21.5	8.5	1.3	1.0	2.62	842	0.354	36.2

2.2 Experimental methods—Low–high pressure gravimetry (LHPG)

A magnetic suspension balance (Losch 1999; Dreisbach et al. 2003) was used to measure the adsorption isotherms of CO_2 (>99.995 purity, Air Liquide) measurement with a microbalance while increasing the gas pressure from 0 to 1200 kPa and for temperature ranging from 323 to 473 K. 1 to 2 g of sample were *in situ* outgassed at 673 K under a constant residual pressure of 10^{-6} kPa before cooling the system to the adsorption temperature. The sample was then exposed to pure CO_2 at a given pressure. After equlibration of the system, the sample weight as well as both pressure and temperature were recorded. The measured mass uptake (the reduced mass Ω) has to be corrected for buoyancy effects to determine the absolute adsorbed amount $m_{absolute}$ (Belmabkhout et al. 2004; Dreisbach et al. 2003) using (1). For this purpose the density of gases is determined experimentally using a titanium cylinder of calibrated volume. By weighing this calibrated volume in a gas or vapour atmosphere the local density of the gas ρ_{gas} is determined as a function of pressure and temperature.

$$\Omega = m_{absolute} - \rho_{gas}(V_{adsorbent} + V_{crucible} + V_{adsorbedphase}) \quad (1)$$

where $V_{adsorbent}$ and $V_{crucible}$ are determined by the helium isotherms method, while $V_{adsorbed\ phase}$ can be extracted from the micropore volume of the sample (Keller and Staudt 2005).

3 Computational methodology

The chemical composition $Si_{136}Al_{56}M_{56}O_{384}$ (with M = Li^+ and Na^+) was chosen in order to reproduce the experimental Si/Al ratio equal to 2.4 for the investigated LiY and NaY samples. The distribution of the extra-framework cations in NaY was modeled as follows, based on the structure refined from neutron diffraction data (Fitch et al. 1986): 6 cations in SI sites located in the hexagonal prism connecting two sodalite cages, 18 in SI' sites in the sodalite cage in front of the six-ring window connected to the hexagonal prism, and 32 in SII sites in the 12-ring windows of the supercages. For LiY, the distribution of the extra-framework cations proposed by Forano et al. (1989) was used, with 24 Li^+ in SI' sites and 32 Li^+ in SII sites. The faujasite host is assumed to be semi-ionic with atoms carrying the following partial charges (in electron units): Si (+2.4), Al (+1.7), O_z (−1.2) consistent with those used for Na and Li (+0.7) as previously reported (Maurin et al. 2005d).

The successful simulation of the CO_2 adsorption in NaY and LiY systems then required an accurate description of the interatomic potential between the carbon dioxide molecules and the zeolite framework, including the extra-framework cations, and between the adsorbate molecules. For carbon dioxide, we used an atomic point charge model with O=C=O angle and C-O bond length of 180° and 1.17 Å respectively, and the following charges (in electron units) assigned to the carbon C (+0.72) and the oxygen O (−0.36) atoms (Maurin et al. 2005d). The adsorbate-zeolite framework and adsorbate-adsorbate repulsion-dispersion interactions were modeled using Lennard-Jones potentials with our previous parameters which successfully reproduced the adsorption properties of the purely siliceous Faujasite form (Maurin et al. 2005a). Due to the presence of extra-framework cations in LiY and NaY, the simulations required an additional contribution to the forcefield, able to reproduce the interactions between these cations and the carbon dioxide. For the Na^+-CO_2 interaction, our recent Buckingham potential derived using *ab initio* cluster calculations was applied (Plant et al. 2007). The same methodology has been used for extracting the Buckingham potential parameters corresponding to the Li^+-CO_2 interaction. Table 2 reports the new set of parameters for Li^+ cation compared to those previously obtained for the Na^+ cation. Full details of the methodology can be found in our previous paper (Plant et al. 2007).

Table 2 Buckingham potential parameters derived by the ab initio calculations for describing the interactions between the Na^+ and Li^+ cation and the carbon dioxide molecules

Buckingham potential $A\exp(-r/\rho) - C/r^6$ Ion pair	A/eV	ρ/Å	C/eV Å^6
Na–C (CO_2)	576.0	3.120	0.0
Na–O (CO_2)	5600.0	4.421	31.8
Li–C (CO_2)	209.0	2.680	0.0
Li–O (CO_2)	4400.0	4.831	25.5

Absolute adsorption isotherms were then computed using a Grand Canonical Monte Carlo calculation algorithm which allows displacements (translations and rotations), creations and destructions. These simulations consisted of evaluating the average number of adsorbate molecules whose chemical potential equals those of the bulk phase for given pressure and temperature. All these simulations were performed at three different temperatures 323 K, 373 K and 473 K using one unit cell of each faujasite system with typically from 4.10^6 to 5.10^6 Monte Carlo (MC) steps. The zeolite structure was assumed to be rigid during the sorption process. This assumption is not so drastic as the flexibility of the lattice more significantly influences the diffusion properties (Demontis and Suffriti 1997). The Ewald summation was used for calculating electrostatic interactions and the short range interactions were calculated with a cutoff distance of 12 Å. Furthermore, as its kinetic diameter (3.3 Å) is much greater than those of the six-ring opening windows of the

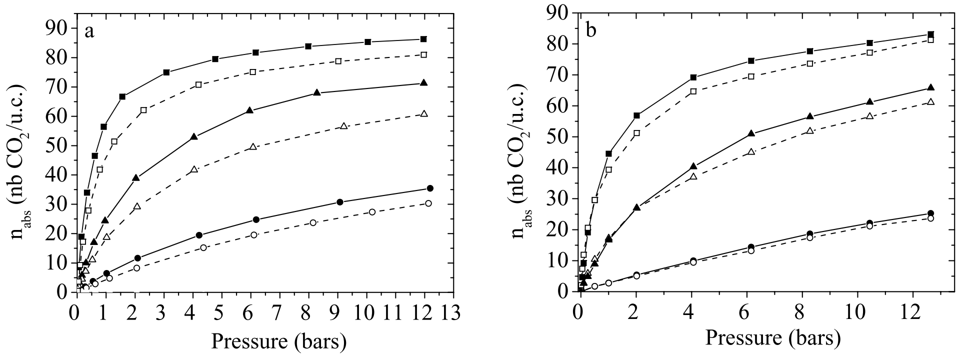

Fig. 1 Experimental (**a**) and simulated (**b**) absolute isotherms for carbon dioxide adsorption in NaY and LiY at various temperatures in the range of pressure 0–12 bars: (□) 323 K, (△) 373 K, (○) 473 K. The *full (empty) symbols* and *solid (dashed) lines* correspond to NaY (LiY)

sodalite cages (2.2 Å), carbon dioxide can not access the sodalite cages. Uncharged dummy atoms with appropriate van der Waals radii were thus placed in these cages to avoid unrealistic introduction of adsorbate molecules during the simulation. The calculation of the differential enthalpies of adsorption at zero coverage $\Delta_{ads}\dot{h}_{\theta=0}$ at the various temperatures was performed through the fluctuations over the number of particles in the system and from fluctuations of the internal energy U (Nicholson and Parsonage 1982) by considering very low pressure:

$$\Delta_{ads}\dot{h} = RT - \frac{\langle U.N\rangle - \langle U\rangle\langle N\rangle}{\langle N^2\rangle - \langle N\rangle^2} \tag{2}$$

In addition both radial distribution functions for $Na^+{-}O(CO_2)$ and $Li^+{-}O(CO_2)$ were calculated from the configurations recorded every 500 steps during the GCMC runs.

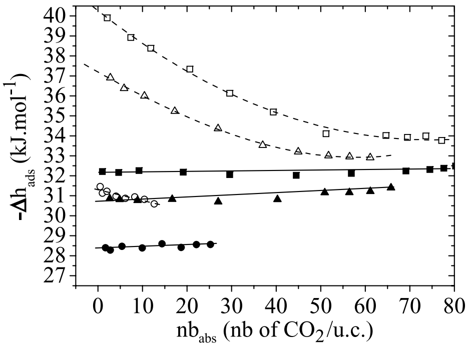

Fig. 2 Evolution of the simulated differential enthalpy of adsorption as a function of coverage at various temperatures in the range of pressure 0–12 bars: (□) 323 K, (△) 373 K, (○) 473 K. The *full (empty) symbols* and *solid (dashed) lines* correspond to NaY (LiY)

4 Results and discussion

Figures 1a and 1b report the absolute isotherms for carbon dioxide adsorption on NaY and LiY obtained both experimentally and theoretically up to 12 bars at three different temperatures 323 K, 373 K and 473 K. It has to be mentioned that this adsorbate slightly deviates from ideal gas behaviour in this domain of pressure and consequently, the simulated data were corrected to take into account this non-ideal state. The experimental one were corrected as well to take into account the buoyancy effect. This correction for the adsorbed phase is negligible in our condition of pressure and temperature. We observe that both the experimental and simulated adsorbed amount of CO_2, strongly decrease when the temperature increases as usually observed in all types of adsorbents (Jaramillo and Chandross 2004; Hirotani et al. 1997; Lee et al. 2002). From both Figs. 1a and 1b, it can be also observed that the adsorption capacity for NaY is only slightly higher than those observed for LiY whatever the considered temperature, as previously pointed out at ambient temperature and in the low domain of pressure (Walton et al. 2006). This result emphasises that substituting Na^+ by Li^+ cations does not drastically affect the CO_2 capacity. Furthermore, the simulated absolute isotherms are in reasonable agreement with those collected experimentally at 323 K and 373 K, whereas at high temperature, the simulated CO_2 amounts are significantly underestimated for both NaY and LiY. However, this relative discrepancy between experiment and simulation is not so crucial, as the new derived force field for representing the interactions between carbon dioxide and lithium cation was not adjusted by matching available experimental CO_2 adsorption data on various Li^+ cation exchanged zeolites via GCMC simulations prior to explore the LiY/CO_2 system, and that the aim of our study is mainly focused on the adsorption mechanism.

Figure 2 reports the simulated evolution of the enthalpies of adsorption as a function of loading for both NaY and LiY. It can be observed that the enthalpies at low coverage are always higher for LiY than for NaY which means that the CO_2 affinity, which can also be estimated from the slope of the theoretical isotherms (Fig. 1b) is higher for LiY than for NaY whatever the considered temperature.

This stronger interaction for LiY can be explained by an average $Li^+{-}O(CO_2)$ distance shorter than the $Na^+{-}O(CO_2)$ analogue, as emphasized by the radial distribution functions for $M^{n+}{-}O(CO_2)$ in Fig. 3. This trend is consistent with those previously reported from experi-

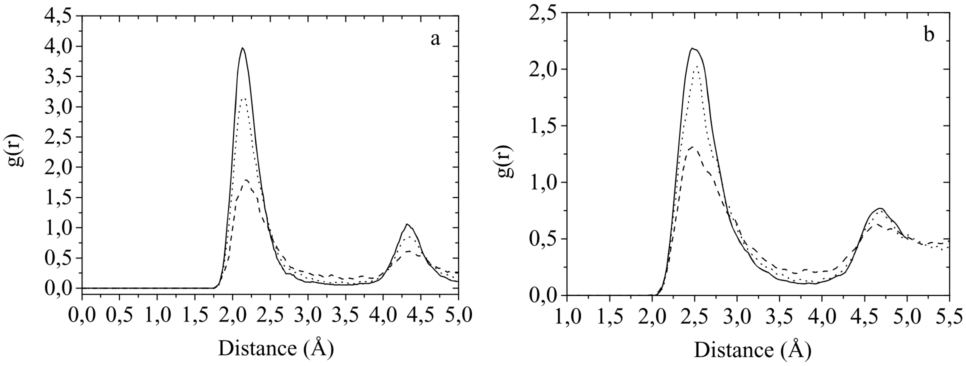

Fig. 3 Radial distribution functions (RDFs): (**a**) $Li^+(SII)–O(CO_2)$ and (**b**) $Na^+(SII)–O(CO_2)$ for 20 carbon dioxide molecules per unit cell estimated at 323 K (*solid lines*), 373 K (*dotted lines*) and 473 K (*dashed lines*) by GCMC simulations for both LiY-CO_2 and NaY-CO_2 systems

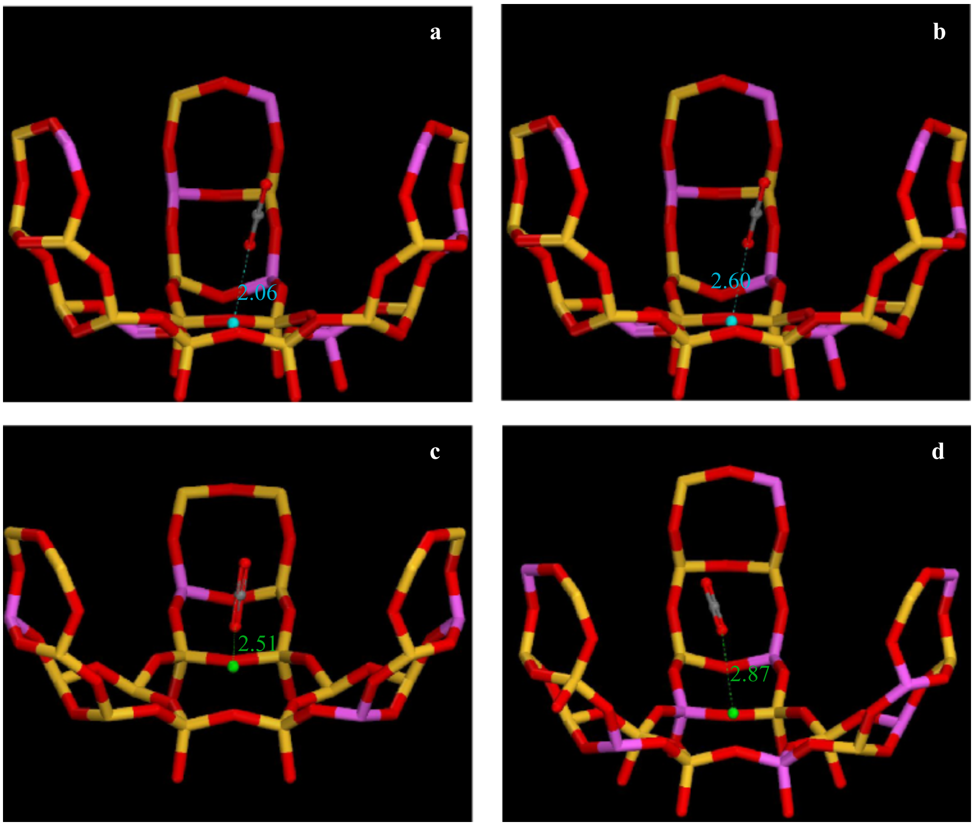

Fig. 4 (Color online) Typical arrangements of the CO_2 molecules in LiY and NaY at low loading depending on the temperature: 323 K (**a**, **c** for LiY and NaY respectively) compared to 473 K (**b**, **d** for LiY and NaY respectively). The Na^+ and Li^+ ions located in SII sites are represented in *green* and *light blue* respectively. The $Li^+–O(CO_2)$ and $Na^+–O(CO_2)$ distances are reported in Å

mental and theoretical results for the adsorption of CO_2 in faujasite X (Barrer and Gibbons 1965) or other gases in various zeolite systems (Bezus et al. 1971; Dzhigit et al. 1971) which has been usually attributed to the strongest polarizing power of Li^+. These simulated enthalpies at the initial stage of adsorption estimated to be -38.4 kJ·mol^{-1} and -31.3 kJ·mol^{-1} at 323 K for LiY and NaY, respectively, are also in good agreement with those previously calculated using a combination of both DFT calculations and microcalorimetry measurements (Plant et al. 2006).

Furthermore, Fig. 2 clearly shows that these values significantly decrease when the temperature decreases from 323 K to 473 K as already shown by Akten in Na-4A (Akten et al. 2003). Similar behaviour has been also pointed out for the adsorption of another quadrupolar gas, N_2 in faujasite X (Barrer and Stuart 1959). This phenomenon can be explained as follows. As the thermal agitation increases, we observe:

(i) a significant deviation from linearity of the ($M^{n+} \ldots$ O=C=O) adduct corresponding to the strongest interaction between the quadrupolar adsorbate and the extra-framework cations.
(ii) a broader distribution of the $M^{n+}–O(CO_2)$ distance as reported by Fig. 3 for both Li^+ and Na^+ which clearly shows that the CO_2 tends to move farther away from the cations and be more delocalized within the supercage of the Faujasite. Illustrations of the larger $M^{n+}–O(CO_2)$ distances are provided in Fig. 4 where we can ob-

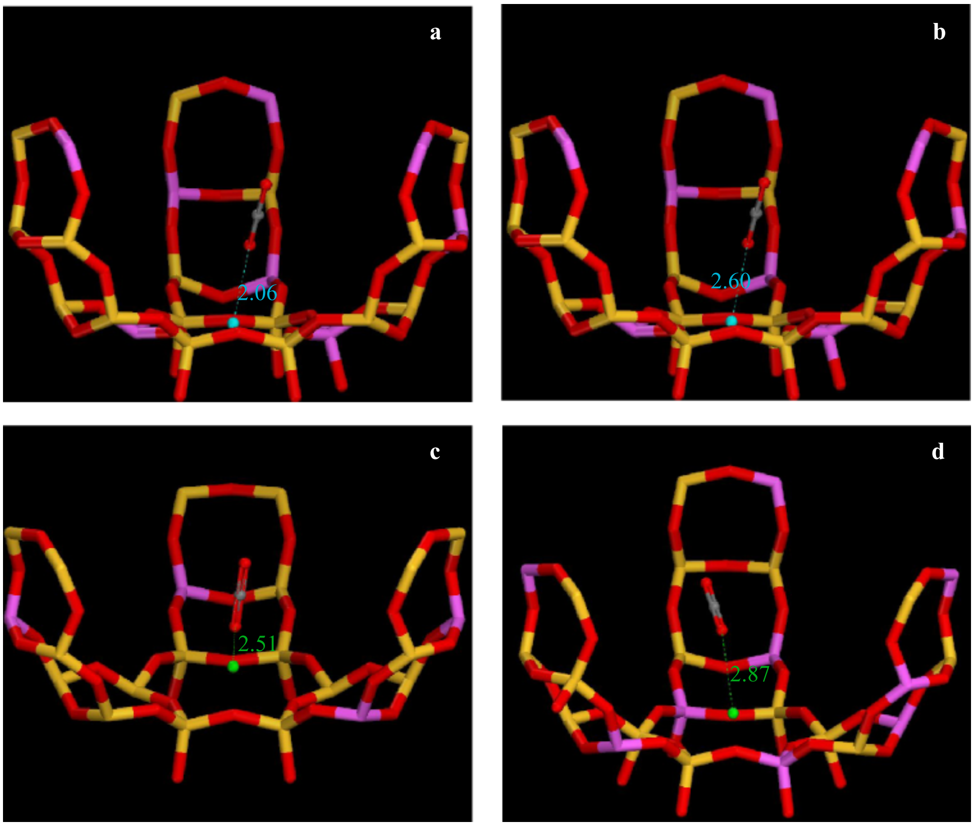

Fig. 5 Typical arrangements of the CO_2 molecules at intermediate and high loadings interacting with a single SII cation site at the same time in LiY (**a**) and NaY (**b**). The $Li^+{-}O(CO_2)$ and $Na^+{-}O(CO_2)$ distances are reported in Å

serve at 473 K that some typical $Li^+{-}O(CO_2)$ and $Na^+{-}O(CO_2)$ distances of 2.60 Å and 2.87 Å respectively are much higher than the average values of 2.06 Å and 2.87 Å at 323 K.

Both effects tend to lower the interaction between the adsorbate molecules and the extra-framework cations leading to a decrease of the differential enthalpies of adsorption.

In addition, the interest in simulating the evolution of such thermodynamic data as a function of the loading relies on the characterisation of the interaction between the adsorbate and the adsorbent surface at the microscopic scale (Llewellyn and Maurin 2005a). Figure 2 clearly shows that for both 323 K and 373 K, the differential enthalpy of adsorption either decreases or remains constant as the loading increases for LiY and NaY respectively. Our previous GCMC simulations (Maurin et al. 2005d) showed that in NaY at the initial stage of loading, the CO_2 molecules are preferentially interacting with Na^+ located in sites SII. As the loading increases, the adsorbate is still interacting with Na^+ cations (in sites SII) which are more and more solvated by the surrounding CO_2 molecules. Indeed, the CO_2/NaY interaction energy is only slightly changed due to the solvation process whereas the CO_2/CO_2 interactions increase. The combination of these two contributions leads to the relative flat profile of the differential enthalpy of adsorption when the loading increases. By contrast, in LiY, the Li^+ cations is more recessed in the six ring windows and consequently it is difficult for a second molecule to approach the SII site as pointed out by Fig. 5a. Such behaviour has been already suggested for explaining the CO adsorption process in MFI (Savitz et al. 2000). It results a large increase of the characteristic $Li^+{-}O(CO_2)$ distances for the second adsorbate molecules interacting with the same SII sites, in contrast to what occurs for Na^+ cation (Fig. 5b), which means that the additional adsorbates do not interact as strongly and induces a pronounced decrease of the CO_2/LiY interaction energy when the loading increases. This contribution, combined with an increase of the CO_2/CO_2 interaction energy, leads to a decrease of the differential enthalpy of adsorption as coverage increases.

At higher temperature (473 K) the enthalpies remain almost unchanged for both faujasites in the whole range of loading which suggest a different CO_2 adsorption mechanism in both Y-Faujasite compared to those pointed out at lower temperature. In this case, the thermal agitation is such that the CO_2 tends to feel an “average homogeneous” adsorbent surface in both cases corresponding to a combination of interactions with both the negatively charged oxygen of the framework and the extra-framework cations leading to a mean constant value of the CO_2/FaujasiteY surface interaction energy. As the number of CO_2 molecules in the supercage is quite limited even at the highest investigated pressure, the energy part of the CO_2/CO_2 interactions remains almost constant. The combination of these two contributions leads to the relative constant value of the differential enthalpy of adsorption when the loading increases. Finally, the resulting enthalpy values for LiY and NaY are between those previously reported for DAY (16–18 kJ·mol^{-1}) (Maurin et al. 2005d) and those calculated at lower temperature for LiY and NaY respectively. It is thus clearly established that the temperature influences the microscopic adsorption mechanism which is consistent with our previous findings on the adsorption of nitrogen in NaX investigated at both 77 K and 302 K (Llewellyn et al. 2005b).

5 Conclusions

A combination of Grand Canonical Monte Carlo simulations and adsorption measurements allowed us to probe the effect of both the nature of the extra-framework cations and the temperature on the CO_2 adsorption behaviour of Y Faujasite systems. It was clearly shown that:

(i) both values and evolutions of the differential enthalpy of adsorption as a function of the loading are mainly governed by the nature of the extra-framework cations and the deviation of the SII cation position from the plane of the six-membered ring.
(ii) the CO_2 adsorption mechanism significantly differs at high temperature (473 K) whatever the considered faujasite Y system.

As we observed some discrepancy between our model and the experimental isotherms, our next step will be to refine our interatomic potential. In addition, LiNaY models will be built with different ion exchange ratio to better understand the role of the co-cation in the adsorption processs.

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