Adsorption (2008) 14: 207–213
DOI 10.1007/s10450-007-9098-1

Adsorption of carbon dioxide in SAPO STA-7 and AlPO-18: Grand Canonical Monte Carlo simulations and microcalorimetry measurements

Irena Deroche · Lucia Gaberova · Guillaume Maurin · Philip Llewellyn · Maria Castro · Paul Wright

Received: 30 April 2007 / Revised: 27 July 2007 / Accepted: 20 December 2007 / Published online: 9 January 2008

Abstract The adsorption properties of carbon dioxide in SAPO STA-7 has been investigated by combining Grand Canonical Monte Carlo simulation and microcalorimetry. The modeling approach, based on both newly derived interatomic potentials for describing the interaction between CO_2 and the Brønsted acid sites, and a realistic description of the silicon distribution within the framework, provides isotherms and evolutions of the differential enthalpy of adsorption as a function of coverage for the STA-7 material characterised by a silicon fraction of 0.19. The simulated results are revealed to be in good agreement with the experimental data that allowed us to provide a possible microscopic mechanism of CO_2 adsorption in this material. These whole results are thus compared to those obtained for the purely aluminophosphate form of the AlPO-18. It is clearly emphasized that distinct adsorption behaviours are observed in these two systems, depending on the energetic characteristics of their surfaces.

Keywords SAPO · STA-7 · AlPO-18 · CO_2 · Adsorption · Grand Canonical Monte Carlo · Microcalorimetry · Isotherms and enthalpies of adsorption

---

I. Deroche · G. Maurin (✉)
Institut Charles Gerhardt Montpellier, UMR 5253
CNRS, ENSCM, Université Montpellier 2, Place E. Bataillon,
34095 Montpellier cedex 05, France
e-mail: gmaurin@lpmc.univ-montp2.fr

L. Gaberova · P. Llewellyn
Laboratoire Madirel UMR CNRS 6121, Université de Provence,
Centre St. Jérôme, 13397 Marseille cedex 20, France

M. Castro · P. Wright
School of Chemistry, University of St. Andrews,
The Purdie Building, North Haugh, St. Andrews, Fife KY16 9ST,
UK

1 Introduction

The separation of CO_2/CH_4 gas mixture is still the subject of many fundamental and industrial research (Liu et al. 2002). One of the main reason is the high decrease of the energy content of the natural gas when an important amount of CO_2 is present (Li et al. 2004). Furthermore, the carbon dioxide, due to its corrosive properties in the presence of water, significantly reduces the natural gas pipelines shelf life (Bolland and Saether 1992). It is thus estimated that the CO_2 content of the natural gas has to be decreased below 2–3% (Li et al. 2004) before passing to the pipeline. Accordingly, since the last few years, a meaningful scientific effort has been devoted to find a suitable solution for removing CO_2 from the natural gas stream. Among the possible procedures, we can mention the absorption of CO_2 in the amine-based systems, currently used for the purification of natural gas on the industrial scale (Tobiesen et al. 2005). However, amine plants being complex and costly to develop, the scientific community has been looking for alternative solutions for both separation/removal and storage of CO_2. Selective adsorption on microporous materials seems to provide another alternative (De Vos and Verweij 1998). Zeolites and derived materials have been shown to be particularly suitable for this application since they combine high CO_2 adsorption capacities, friendly environment, and both thermal and mechanic stability.

SAPOs, which belong to the class of “zeolite-like” materials, have been firstly synthesized in early 80’s (Lok et al. 1984). These silicoaluminosphate systems obtained by introducing silicon atoms within the electrically neutral AlPO framework are characterized by the presence of Brønsted acide sites which provides to these materials specific adsorption and catalytic properties (Olsbye et al. 2005). Recent studies on these systems showed their excellent abilities for the CH_4/CO_2 separation (Poshusta et al. 2001; Li et al. 2004). The gas selectivity in these SAPO materials is governed by both the steric effect, as they usually exhibit pore size comparable to those of the adsorbate molecules, and the strength and nature of the interactions between each adsorbate and the framework. This behaviour slightly deviates from those pointed out in classical aluminosilicate zeolites (FAU, MFI) (Jia et al. 1994) where the latter criteria plays the predominant role in the separation properties. In some typical cases, the selectivity of a SAPO membrane can be three times higher than those usually observed in the aluminosilicates (Li et al. 2004). Here, we focus on the CO_2 adsorption properties of the SAPO STA-7 material recently synthesized by the St. Andrews group (Wright et al. 2000), by combining molecular simulations and microcalorimetry measurements. The first step of this work consists of building a realistic structural model of the STA-7 framework characterized by an atomic silicon fraction close to those of the experimental sample. This is done by using the conclusions drawn in our recent studies based on energy minimization techniques and ^{29}Si MAS NMR (Déroche et al. 2008). It was clearly established that in such range of silicon content, the silicon distribution follows a non-random mechanism preferentially generating isolated Si-Al-Si pairs with two silicon atoms located in the same four-membered rings, this arrangement being stabilized by the interaction between the Brønsted acid sites. From this selected configuration, Grand Canonical Monte Carlo (GCMC) simulations based on atomistic potential parameters and a partial charge model, are then performed to establish a correlation between the microscopic behavior of the SAPO/adsorbate system and the equilibrium thermodynamic properties. We report a new self consistent set of potential parameters for representing the interaction between CO_2 and the Brønsted acide sites, derived by using *ab initio* cluster approach (Plant et al. 2007). Both the simulated isotherms and enthalpies of adsorption are then compared to those measured by microcalorimetry in a wide range of pressure, in order to test the validity of both the derived force fields and the microscopic model of the framework. Once, we get a reasonable agreement with the experimental data, the following step consists of exploring the preferential adsorption sites and thus emphasizing the microscopic mechanisms for CO_2 adsorption in STA-7 materials consistent with the corresponding evolution of the differential enthalpy of adsorption as a function of coverage. This behaviour is then compared to those obtained in the purely aluminophosphate AlPO-18 form, which shows a similar structure than those of the STA-7, in order to estimate the influence of the presence of the Brønsted acide sites on the adsorption process.

2 Computational methodology

2.1 Material

The frameworks of both AlPO-18 and SAPO STA-7, related to the AEI and SAV structure types (Meier and Olson 1978) respectively, can be described as chains of tilted double six-membered rings (D6R). The structure of the recently synthesized SAPO STA-7 material (Wright et al. 2000) exhibits an arrangement of two distinct pore channels, both situated along the [001] direction, each constrained by eight-membered rings (Fig. 1a) with diameters of 6.93 Å and 6.21 Å for the large (A) and small (B) channels respectively. By contrast, the AlPO-18 structure (Simmen et al. 1991) exhibits a regular three-dimensional eight-membered ring channel system, with only one channel size in the [001] direction, corresponding to diameters of 7.2 × 6.7 Å.

The crystal structures of both materials were modelled as follows: the AlPO-18 structure was built from Rietvelt refined crystallographic data (Simmen et al. 1991) and geom-

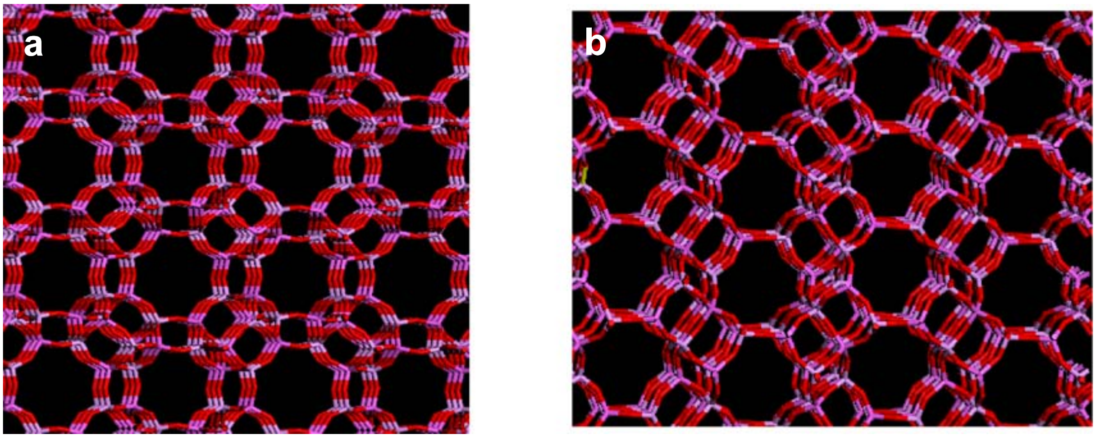

Fig. 1 Structure of STA-7 (**a**) showing the large (A) and small (B) eight-membered rings channels, and AlPO-18 (**b**) with its uniform system of eight-membered rings

etry optimized using energy minimization technique implemented in GULP (Gale 1997). For SAPO STA-7 material, the pure AlPO form was selected from previous X-ray diffraction data (Wright et al. 2000). To reproduce the experimental silicon fraction of 0.19, we introduced 9 silicon atoms per unit cell, following our previous methodology (Déroche et al. 2008). This method allowed us to select the most stable configuration where the silicon atoms are preferentially located in the same four-membered rings with favorable interaction between the Brønsted acid sites.

Both structures are assumed to be semi-ionic with atoms carrying partial charges. The following set of charges (in electron units) was adopted for the AlPO-18: Al (+1.4), P (+3.4) and O (−1.2), which is currently considered in purely aluminophosphate materials (Kramer et al. 1991). The charge distribution within the framework of STA-7 was defined as follows: the charges on aluminium, phosphorous and their surrounding oxygen atoms labelled O_P, were the same than those considered in AlPO-18. The charge on the proton was estimated to be +0.55 from our own DFT calculations (Déroche et al., submitted) which is consistent with those already reported in the literature for other SAPO materials (Shah et al. 1997). We then introduced distinct charges on the two other types of oxygen, O_s (−1.1) and O_b (−1.0), corresponding to oxygen atoms bonded to the Si atoms, with O_b hosting the proton. The charge on the Si (+2.35) was defined with the constraint of a global neutral charge for the STA-7 framework.

2.2 Grand Canonical Monte Carlo simulations

The successful simulation of the CO_2 adsorption in both AlPO-18 and STA-7 systems requires first an accurate description of the interatomic potential between the carbon dioxide molecules and the zeolite framework, including the protons, and between the adsorbate molecules. For carbon dioxide, we used an atomic point charge model with the following charges (in electron units) assigned to the carbon C (+0.72) and the oxygen O (−0.36) atoms (Maurin et al. 2005a). Both 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 various Faujasite forms (Maurin et al. 2005b). Due to the presence of the proton in STA-7, the simulations required an additional contribution to the forcefield, able to reproduce the interactions between these protons and the carbon dioxide. For the H^+–C (CO_2) and H^+–O (CO_2) interactions, we performed *ab initio* cluster calculations following the same methodology we used for extracting the Buckingham potential parameters (Plant et al. 2007) for the Na^+–CO_2 pair. Table 1 reports the new set of Buckingham potential parameters for the H^+–CO_2 interaction. Full details of the calculations can be found elsewhere (Déroche et al., submitted).

Table 1 *Ab-initio* derived Buckingham potential parameters for the H^+–CO_2 pair

Buckingham potential $A\exp(-r/\rho) - C/r^6$

Ion pair	A/eV	ρ/Å	C/eV Å^6
H–C (CO_2)	58.0	2.50	0.0
H–O (CO_2)	1748.0	4.68	16.6

Absolute adsorption isotherms were then computed using a Grand Canonical Monte Carlo algorithm, implemented in the Accelerys Cerius2 programme (Cerius2 1999). 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. We performed all simulations at 303 K using a simulation box of a double unit cell $(1, 1, 2)$ for both AlPO-18 and STA-7. We have typically performed this simulation along 2.5×10^6 Monte Carlo steps. We have monitored the equilibrium conditions by plotting the evolution of the total energy over the MC steps. In all the calculations, the adsorbent lattice was considered rigid. The Ewald summation was used to calculate the electrostatic interactions, with the cut-off distance fixed at the value of 9.5 Å. In order to estimate the differential enthalpy of adsorption, we performed the calculation through the fluctuation over the number of particles in the system and from the internal energy.

3 Experimental

The STA-7 material was synthesized in its acid version with a silicon fraction of about 0.19. Full details of the experimental conditions can be found elsewhere (Wright et al. 2000). The AlPO-18, prepared in its purely aluminophosphate form was kindly provided for our microcalorimetry experiment by the Department of Chemistry and Catalysis of the Utrecht University.

Prior to each adsorption experiment, the sample is outgassed using sample-controlled thermal analysis (SCTA). The samples were thus heated using SCTA conditions; under a constant residual vacuum pressure of 0.02 mbar up to final temperatures of 200°C for AlPO-18 and 300°C for the STA-7 sample, which were maintained until the residual pressure, was less than 5×10^{-3} mbar. The adsorption at 303 K up to 15 bar and 30 bar for AlPO-18 and STA-7 material respectively, was carried out by means of a Tian-Calvet type isothermal microcalorimeter coupled with a manometric device built *in-house*. This microcalorimeter consists of two thermopiles mounted in electrical opposition. Each thermopile is comprised of around 900 chromel-alumel thermocouples (Llewellyn and Maurin 2005). This complete apparatus allowed us to obtain both the absolute isotherms and the differential enthalpies of adsorption as a function of coverage in both STA-7 and AlPO-18 systems. Furthermore, for such studies performed at ambient temperature and high pressure, an appropriate expression for the gas-non ideality was included using the Peng Robinson equation of state (Peng and Robinson 1976). Finally, a point-by-point adsorptive dosing procedure detailed elsewhere (Llewellyn and Maurin 2005) was used to evaluate pseudo-differential enthalpy of adsorption noted $\Delta_{ads}\dot{h}$ with a maximum error bar of 0.5 kJ mol^{-1} in the whole range of pressure. The carbon dioxide with 99.995% of purity was obtained from Air Liquide (Alphagaz, France).

4 Results and discussion

Figure 2a reports the absolute isotherms for CO_2 adsorption in AlPO-18 and SAPO STA-7 obtained by both microcalorimetry and GCMC simulations at 303 K. As CO_2 usually does not behave as an ideal gas in the considered range of pressure, the experimental as well as the simulated data were corrected to take into account this non-ideal state. One can observe that the simulated absolute isotherm matches the experimental one for AlPO-18 and slightly underestimates the experimental loading for the STA-7 material in the whole range of pressure. However, the difference between experimental and simulated loading never exceeds 7%. This agreement simulation-experiment is reasonable when one considers that the sample surely contains some impurities and structural defects that are not taken into account in our simulations. Furthermore, the saturation capacities can be estimated to be about 14 and 22 CO_2 molecules per unit cell for AlPO-18 and SAPO STA-7 respectively. Since both the model and the experimental sample of STA-7 contain almost 9 silicon atoms and consequently 9 associated proton per unit cell, the difference observed between the capacity of adsorption for the two structures would come from the additional available Brønsted acide sites corresponding to preferential adsorption sites for CO_2.

It is well established that from the slope of the adsorption isotherm in the initial domain of pressure, it is possible to estimate the adsorbate affinity for a given adsorbent. As we can observe from Fig. 2a, the mentioned slope is clearly much higher for STA-7 than for AlPO-18. This result is explained by the presence of the Brønsted acid sites in STA-7, which gives rise to more energetic adsorption sites for the quadrupolar CO_2 adsorbate. This outcome is consistent with the experimental and simulated values of the differential enthalpy of adsorption at low coverage, which can be estimated from Fig. 2b. It can be observed that the experimental values are −38.0 kJ mol^{-1} and −25.5 kJ mol^{-1} for STA-7 and AlPO-18 respectively. This energy difference is very similar to what can be observed between a purely siliceous zeolite and a protonated form when one considers the adsorption of quadrupolar gases (Dunne et al. 1996).

Furthermore, the interest in measuring the evolution of the differential enthalpies of adsorption as a function of coverage relies on the characterisation of the adsorbent surface with respect to a given adsorbate. It is well established that a decrease of the differential enthalpy of adsorption as a function of the gas loading can be ascribed to a heterogeneous adsorbent and that a flat profile corresponds to a balance between increasing adsorbate-adsorbate interactions and an energetic heterogeneity of the adsorbent surface. By contrast, an increase in the differential enthalpy of adsorption reveals a relatively homogeneous environment for adsorbate/adsorbent interactions.

The CO_2 adsorption in AlPO-18 is a typical example where the adsorbate interacts with a homogeneous ener-

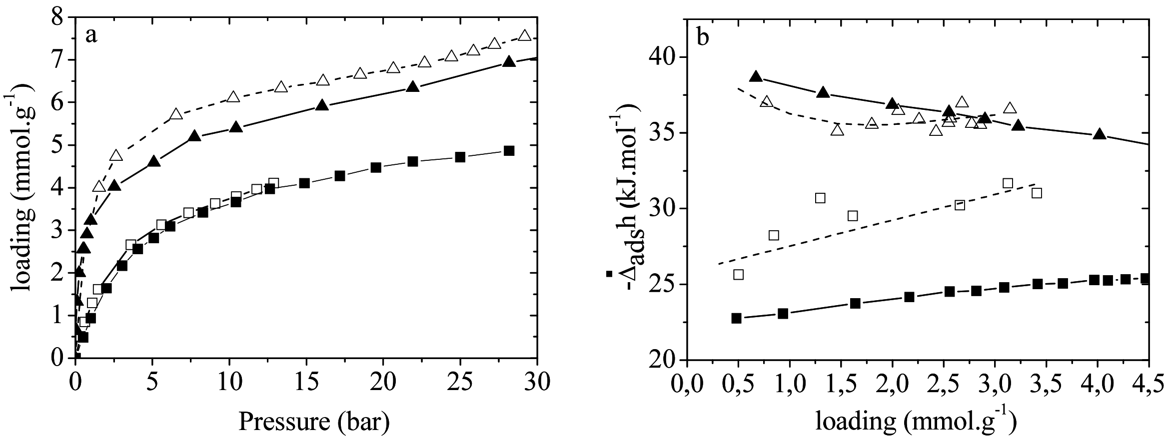

Fig. 2 Experimental (*empty symbols*) and simulated (*full symbols*) absolute isotherms (**a**) and differential enthalpies of adsorption ($\Delta_{ads}h$) as a function of the coverage (**b**) for CO_2 adsorption in AlPO-18 (*square symbols*) and STA-7 (*triangle symbols*)

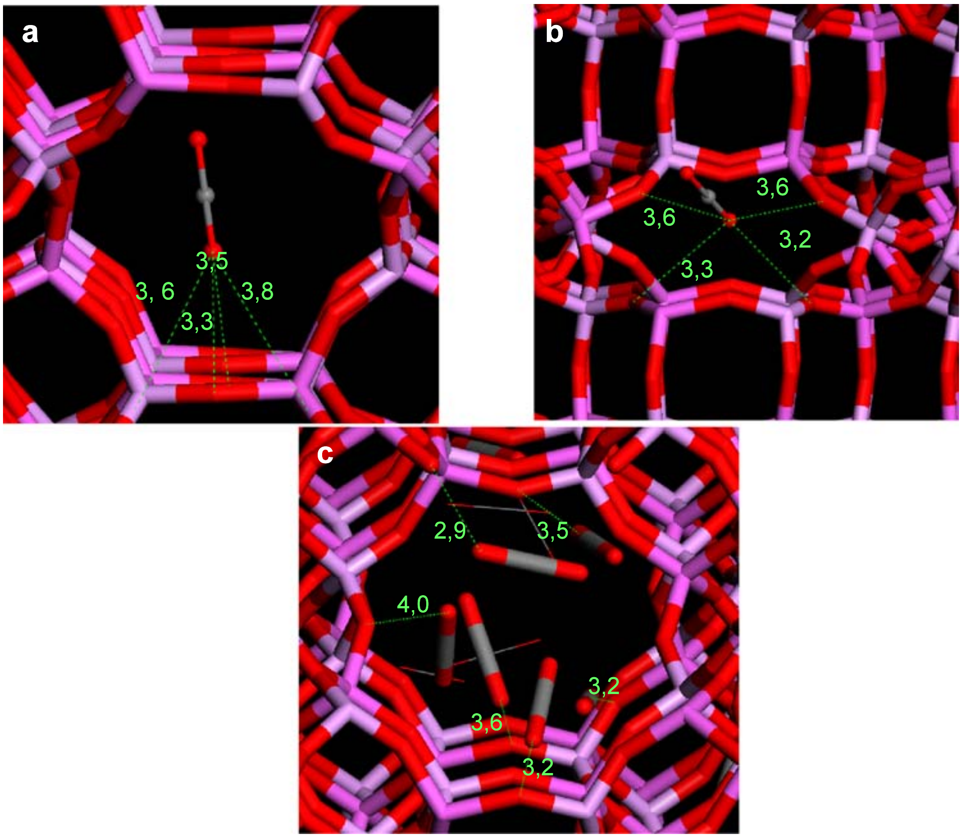

Fig. 3 Illustration of the preferential adsorption site for CO_2 in AlPO-18 at low loading: a four-membered ring (**a**) or an eight-membered ring window (**b**). Typical arrangement of CO_2 molecules in AlPO-18 at high loading (30 bars) (**c**). The corresponding distances are reported in angstroms

getic surface and thus leads to an increasing differential enthalpy profile, concluded from both experimental and computational evidences (Fig. 2b). In this case, the absence of Brønsted acids would mean that there are no preferential adsorption sites within the pore, and that the adsorption surface experienced by the adsorbate molecules can be described as being homogeneous. Our simulations confirm this assumption. Although some interaction between the CO_2 and the oxygen of the framework may be seen, typically in the vicinity of a four-membered or a eight-membered rings (Fig. 3a and Fig. 3b), we can not define specific adsorption sites. We observe that the CO_2 molecules are most probably situated in the centre of the cavities, i.e. more-or-less homogeneously distributed within the cages, with characteristic distances separating the oxygen of the CO_2 molecule and the oxygen of the framework generally ranged from 2.8 to 3.3 Å, as reported in Fig. 3c. Our simulations also showed that the mean distance between oxygen of the framework and oxygen of the carbon dioxide remains almost unchanged when the loading increases whereas those between the carbon dioxide molecules, d(C–C), become significantly shorter, leading to an increase of the adsorbate-adsorbate interaction energy. Indeed, carbon dioxide probes AlPO-18 as an homogeneous energetic surface with an almost constant CO_2/adsorbent interaction energy and CO_2/CO_2 contribution increasing with loading, thus leading to an increase in the differential enthalpy of adsorption with coverage as reported in Fig. 2b. This result is consistent with similar enthalpy profile observed for the adsorption of CO_2 in purely siliceous zeolites such as silicalite (Choudary and Mayadevi 1996; Dunne et al. 1996; Hampson and Rees 1993) or DAY (Maurin et al. 2005b), presenting as well a homogeneous energetic surface.

By contrast, the investigated SAPO STA-7 material exhibits a significant decrease of the differential enthalpy of adsorption at the initial stage of loading followed by a smooth profile for higher pressure (Fig. 2b). This profile is only partially reproduced by our simulations which predict a continuous decrease of the enthalpy in the range of investigated pressure. This discrepancy should be most probably due to the presence of other types of silicon arrangements in the material, for instance Si dispersed phase, than only the aluminosilicate isolated pairs considered in our simulations. The influence of such geometric consideration on the enthalpy profile will be discussed in future paper (Déroche et al., submitted). It has to be noticed that the simulated values are within the same order of magnitude than those obtained by experiments, which validates the interatomic potentials and the microscopic model for describing the STA-7 framework. According to what has been claimed just above, the energetic surface of this material thus presents a significant heterogeneity. It means that the preferential Brønsted

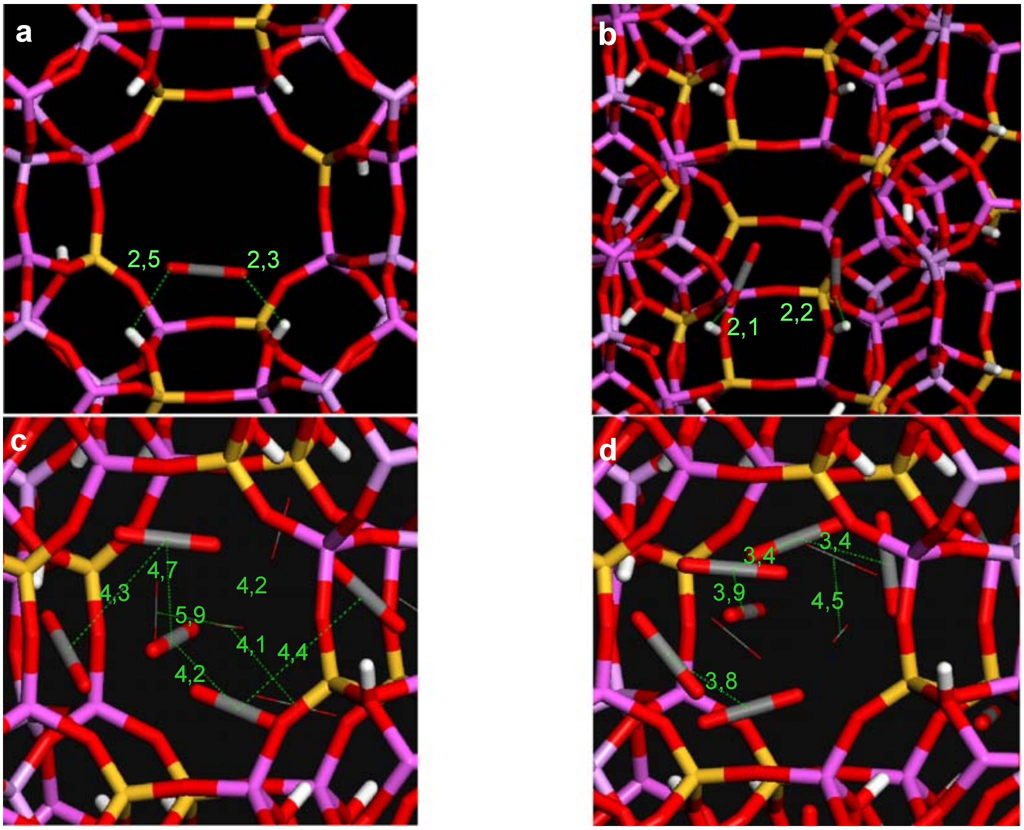

Fig. 4 Most stable CO_2 geometries involving the aluminosilicate isolated pairs (**a**). Typical arrangements of the CO_2 molecules in the large cage of the SAPO STA-7 at low (0.25 bar) (**b**), intermediate (2.5 bars) (**c**) and high (25 bars) loading (**d**). The resulting distances reported in angstroms

acid sites, generated by the as-called aluminosilicate isolated pairs, occupied by the CO_2 molecules at the initial stage of loading, are saturated when the loading increases and consequently the CO_2 molecules occupy less energetic sites which leads to a decrease of the CO_2/adsorbent interaction energy. 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 in our simulation data. Illustration of this result is provided in Fig. 4. As we stated above, the silicon atoms are distributed in a such a way to form the as-called aluminosilicate isolated pairs, corresponding to the association of two Brønsted acid sites, located on one four-membered ring. Such (Si,H^+) arrangement provides favourable adsorption sites, allowing the CO_2 molecule to form a double "both-ends" interaction at the initial stage of loading, as illustrated in Fig. 4a. When the loading increases, we do not see anymore this preferential geometry, since each proton is interacting with a single molecule of CO_2 as illustrated in Fig. 4b. Besides, we provide typical arrangements of CO_2 molecules at intermediate (Fig. 4c) and high (Fig. 4d) loadings. The smooth enthalpy profile observed by microcalorimetry over 1 $\text{mmol}\,\text{g}^{-1}$ could be explained by the fact that the sample should also contain some silicon dispersed arrangement which would be probed by CO_2 as a more or less homogeneous energetic environment leading to similar values for the adsorption enthalpy.

5 Conclusion

The adsorption properties of AlPO-18 and SAPO STA-7 materials were investigated using GCMC simulations based on newly derived potential, combined to microcalorimetry. A good agreement between experiment and simulation was achieved, such validating the accuracy of the newly derived force field for describing the interaction between the proton and the CO_2 molecules. The combination of modelling and experimental approaches allowed us to provide a microscopic adsorption mechanism of both STA-7 and AlPO-18 consistent with the experimental findings. Two distinct behaviours were observed: the CO_2 first probes AlPO-18 as an homogeneous energy surface, without preferential adsorption sites, leading to an increase of differential enthalpy profile. By contrast, the STA-7 material can be seen as a heterogeneous energetic surface, with some preferential adsorption sites at the initial stage of loading, formed by the Brønsted acid sites arranged within aluminosilicate isolated pairs. When the loading increases, these attractive sites become saturated, and the CO_2 molecules have to occupy less energetic sites, that leads to the decrease of the differential enthalpy experimentally observed in the low domain of pressure. We report elsewhere a further investigation for elucidating the role of both the silicon distribution and the silicon content on the adsorption of CO_2 in STA-7.

Acknowledgements This work was supported by EU funding via FP6-Marie Curie Research Training Network "INDENS" (MRTN-CT-2004-005503).

References

Bolland, O., Saether, S.: New concepts for natural gas fired power plants which simplify the recovery of carbon dioxide. Energy Convers. Manag. **33**, 467–475 (1992)

Cerius2, v. 4.2. Accelrys, Inc., San Diego (1999)

Choudary, V.P., Mayadevi, S.: Adsorption of methane, ethane, ethylene and carbon dioxide on silicalite. Zeolites **17**, 501–507 (1996)

Déroche, I., Maurin, G., Llewellyn, P.L., Castro, M., Wright, P.A.: Silicon distribution in SAPO materials: a computational study of STA-7 combined to ^{29}Si MAS NMR spectroscopy. Micropor. Mesopor. Mater. **107**, 268–275 (2008)

Déroche, I., Gaberova, L., Maurin, G., Llewellyn, P.L., Castro, M., Wright, P.: Influence of both (Si,H^+) arrangement and silicon content on the adsorption of CO_2 in SAPO STA-7: Grand Canonical Monte Carlo simulations and microcalorimetry. J. Phys. Chem. C (submitted)

De Vos, R.M., Verweij, H.: Improved performance of silica membranes for gas separation. J. Membr. Sci. **143**, 37–51 (1998)

Dunne, J.A., Marivala, R., Rao, M., Sircar, S., Gorte, J., Meyers, A.L.: Calorimetric heats of adsorption and adsorption isotherms. 1. O_2, N_2, Ar, CO_2, CH_4, C_2H_6 and SF_6 on silicalite. Langmuir **12**, 5888–5895 (1996)

Hampson, L.A., Rees, L.V.C.: Adsorption of ethane and propane in silicalite-1 and zeolite NaY—determination of single components, mixture and partial adsorption data using an isosteric system. J. Chem. Soc. Dalton Trans. **89**, 3169–3176 (1993)

Gale, J.: A computer program for the symmetry-adapted simulation of solids. J. Chem. Soc. Dalton Trans. **93**, 629–637 (1997)

Jia, M.D., Chen, B., Noble, R.D., Falconer, J.L.: Ceramic zeolite composite membranes and their application for separation of vapor/gas mixtures. J. Membr. Sci. **90**, 1–10 (1994)

Kramer, G.J., Farragher, N.P., van Beest, B.W.H., van Santen, R.A.: Interatomic force-fields for silicas, aluminophosphates, and zeolites—derivation based on ab-initio calculations. Phys. Rev. B **43**, 5068–5080 (1991)

Li, S., Falconer, J., Noble, R.D.: SAPO-34 membranes for CO_2/CH_4 separation. J. Membr. Sci. **241**, 121–135 (2004)

Liu, B.S., Gao, L.Z., Au, C.T.: Preparation, characterization and application of a catalytic NaA membrane for CH_4/CO_2 reforming to syngas. Appl. Catal. A-Gen. **235**, 193–206 (2002)

Llewellyn, P.L., Maurin, G.: Gas adsorption microcalorimetry and modelling to characterise zeolites and related materials. C.R. Chim. **8**, 283–302 (2005)

Lok, B.M., Messina, C.A., Patton, R.L., Gajek, R.T., Cannan, T.R., Flanigen, E.M.: Silicoaluminophosphate molecular-sieves—another class of microporous crystalline inorganic solids. J. Am. Chem. Soc. **106**, 6092–6093 (1984)

Maurin, G., Llewellyn, P.L., Bell, R.G.: Adsorption mechanism of carbon dioxide in faujasites: Grand Canonical Monte Carlo simulations and microcalorhnetry measurements. J. Phys. Chem. B **109**, 6084–16091 (2005a)

Maurin, G., Bell, R.G., Kuchta, B., Lllewellyn, P.L., Poyet, T.: Adsorption of non polar and quadrupolar gases in siliceous faujasite: molecular simulations and experiments. Adsorption **11**, 331–336 (2005b)

Meier, W.M., Olson, D.H.: Atlas of Zeolite Structures, Structure Commission of the International Zeolite Association. Elsevier, Amsterdam (1978)

Olsbye, U., Bjorgen, M., Svelle, S., Lillerud, K.P., Kolboe, S.: Mechanistic insight into the methanol-to-hydrocarbons reaction. Catal. Today **106**, 108–111 (2005)

Peng, D., Robinson, D.B.: New 2-constant equation of state. Ind. Eng. Chem. Fund. **15**, 59–64 (1976)

Plant, D.F., Maurin, G., Deroche, I., Llewellyn, P.L.: Investigation of CO_2 adsorption in Faujasite systems: Grand Canonical Monte Carlo and molecular dynamics simulations based on a new derived Na^+–CO_2 force field. Micropor. Mesopor. Mater. **99**, 70–78 (2007)

Poshusta, J.C., Noble, R.D., Falconer, J.L.: Characterization of SAPO-34 membranes by water adsorption. J. Membr. Sci. **186**, 25–40 (2001)

Shah, R., Gale, J.D., CM Payne, M.: Comparing the acidities of zeolites and SAPOs from first principles. Chem. Commun. **1**, 131–132 (1997)

Simmen, A., McCusker, L.B., Baerlocher, Ch., Meier, W.M.: The structure determination and Rietvelt refinement of the aluminophosphate $ALPO_4$-18. Zeolites **11**, 654–661 (1991)

Tobiesen, F.A., Svendsen, H.F., Hoff, K.A.: Desorber energy consumption amine based absorption plants. Int. J. Green Energy **2**, 201–215 (2005)

Wright, P.A., Maple, M.J., Slawin, A.M.Z.: Cation-directed syntheses of novel zeolite-like metalloaluminophosphates STA-6 and STA-7 in the presence of azamacrocycle templates. J. Chem. Soc. Dalton Trans. **8**, 1243–1248 (2000)