Adsorption of Non Polar and Quadrupolar Gases in Siliceous Faujasite: Molecular Simulations and Experiments

GUILLAUME MAURIN*

Laboratoire Madirel UMR CNRS 6121, Université de Provence, Centre St Jérôme, 13397 Marseille Cedex 20

maurin@up.univ-mrs.fr

ROBERT BELL

The Davy Faraday Research Laboratory, Royal Institution of Great Britain, London W1S 4BS, UK

BOGDAN KUCHTA, THOMAS POYET AND PHILIP LLEWELLYN

Laboratoire Madirel UMR CNRS 6121, Université de Provence, Centre St Jérôme, 13397 Marseille Cedex 20

Abstract.   The adsorption of non polar (argon, methane) and quadrupolar (carbon dioxide, nitrogen) gases on siliceous Faujasite at ambient temperature and high pressure conditions up to 50 bar, is investigated both experimentally and theoretically by combining Microcalorimetry and Grand Canonical Monte Carlo techniques. The aim of this present work is to evaluate the adsorption isotherms as well as the evolution of the differential enthalpies of adsorption as a function of coverage, for each of the gases under study, and to compare directly results of simulations with our own experimental data. To this purpose, the choice of reliable interatomic potentials required to describe both the adsorbate/framework and adsorbate/adsorbate interactions is crucial. This work is thus based on new transferable pair potential models for methane and carbon dioxide, recently developed by one of the authors using quantum mechanical methods. Finally, we propose a simplified model which can relate the differential enthalpy of adsorption at low coverage to the polarisability of the gases.

1. Introduction

Zeolite microporous materials are involved in a large domain of chemical science and technology including catalytic (Corma, 2003) and separation processes, gas storage and ion exchange (Ackley et al., 2003). Many research efforts performed both experimentally and theoretically have been thus focused on this class of materials. This is not only because of their technological importance but also because they represent model systems. Indeed, zeolite materials, which are well-ordered nanoporous materials offer numerous possibilities for

investigating their adsorption properties as a function of many parameters such as size and shape of the pores, chemical composition of the framework (Si/Al ratio, metal substituted aluminophosphate) and nature of the extra-framework cations.

The faujasite system which is an aluminosilicate zeolite, investigated in this paper, has a wide range of industrial applications, partly because of its large pore size and void volume. Its adsorption and catalytic properties depend strongly on the chemical nature as well as the nature and location of the exchangeable cations. Furthermore, it is easy to change the degree of energetic heterogeneity of the faujasite surface by modifying the Si/Al ratio. In this way, we can obtain a homogeneous

*To whom correspondence should be addressed.

adsorbent with the purely siliceous faujasite $Si_{192}O_{384}$ and heterogeneous materials such as Fau-X and Fau-Y, characterised by different Si/Al ratios. Microcalorimetry which has been extensively applied to characterise both the adsorbent and various adsorbent/adsorbate interactions, is a powerful tool to reveal the degree of energetic heterogeneity of gas-solid interactions by following the evolution of the differential enthalpies of adsorption as a function of the gas coverage (Rouquerol et al., 1999). Several experimental studies have been published dealing with the influence of polar and non polar gases characterised by increasing size or magnitude of the quadrupole moment on the adsorption properties of various zeolite systems (Kiselev et al., 1981; Karavias et al., 1991; Dunne et al., 1996).

Over the last few years, molecular simulation of adsorption phenomena has been intensively implemented in order to establish a correlation between the microscopic behaviour of the zeolite/adsorbate and the macroscopic properties which are measured experimentally such as isotherms and enthalpies of adsorption (Nicholson, 1996). Various theoretical methods have been applied in studying adsorption in zeolites including energy minimisation, Monte Carlo and Molecular Dynamic simulations (Fuchs et al., 2001). They rely on accurate interatomic potentials needed to reproduce as closely as possible, the interactions between the adsorbate and the zeolite framework and between the adsorbate themselves. Several efforts are thus concentrated on the development of new reliable pair potentials by using quantum mechanical methods, which have to be then transferable to any zeolite structure.

Our first aim was then to investigate the interactions of a series of non polar (argon, methane) and quadrupolar (nitrogen, carbon dioxide) gases on a homogeneous adsorbent at ambient temperature by combining an original microcalorimetry approach at high pressure and a Grand Canonical Monte Carlo technique. The dealuminated Y zeolite (DAY) material, which is the siliceous form of Faujasite provides a relatively homogeneous energetic environment for gases under study and serves as starting point for future investigation of the effect of energetic heterogeneity on equilibrium properties. This work allowed us to validate two new transferable potentials developed by one of the authors (Bell, 2004) for modelling the interactions between both methane/zeolite and carbon dioxide/zeolite by a direct comparison between simulated isotherms and differential enthalpies of adsorption with experimental ones recorded up to 50 bars. As far as we

know, it is the first time that an interatomic potential describing carbon dioxide in zeolite system has been able to reproduce well the experimental data over such a wide range of pressure. Furthermore, another part of our work was to propose a simplified model based on physical properties of the involved species, in order to explain the evolution of the differential enthalpy of adsorption at low coverage as a function of both the nature of the gas (with fixed zeolite framework) and the type of the extra-framework cations (with fixed gas and monovalent and bivalent cation containing X-Faujasite). We have thus shown for the first time that the variation of chemical hardness of the extra-framework cations can account for the experimental evolution of the differential enthalpy for argon/X-Faujasite system (Maurin et al., 2004). Here, we report that the trend observed for the differential enthalpy of the sorbent/DAY systems can be explained from the polarisabilities of theses gases.

2. Experimental

The dealuminated Y zeolite (DAY) used in this investigation corresponds to the highly siliceous form of Faujasite. This structure consists of large cavities (supercages) which have roughly spherical symmetry and diameter around 12.5 Å. Each cavity is connected to four others in a tetrahedral arrangement. The structure also contains sodalite cage units linked together by double six rings. The sample was obtained by dealumination treatment via a steaming process and was carefully characterised. The chemical analysis gave the following composition: $Na_{1.9}Al_{1.9}Si_{190.1}O_{384}$ (Si/Al ratio = 100), the X-ray diffraction pattern and the morphology observed by Scanning Electron Microscopy being in good agreement with those usually reported for this material. It has to be emphasized that the texture of the surface is slightly different with those observed for X-Faujasite system which means that possible textural defects have been created by the dealumination process.

Prior to each adsorption experiment, the sample was outgassed using Sample Controlled Thermal Analysis, SCTA (Rouquerol et al., 1999). The pure gas adsorption properties of this adsorbent were then investigated at ambient temperature (300 K) up to 50 bars for a series of non polar (Ar, CH_4) and quadrupolar gases (N_2, CO_2). This study was performed by coupling a Tian-Calvet type isothermal microcalorimeter and a manometric device built in house. This apparatus

allowed us to obtain both the isotherms and the pseudo differential enthalpies of adsorption for each gas under study. It has to be mentioned that all the reported experimental data will correspond to absolute adsorption obtained from the correction of the primary excess values as following for ideal gases:

$$n^{\mathrm{a}} = n^{\sigma} + \frac{p.V^{\mathrm{zeo}}}{RT} \qquad (1)$$

where n^a and n^σ are the absolute and excess amount adsorbed respectively and V^{zeo} is the micropore volume of the DAY sample estimated to be 0.342 cm³.g⁻¹ from a t-plot of nitrogen physisorption measurement at 77 K. However for such studies at ambient temperature and high pressure, an appropriate expression for gas non ideality was included using the Redlich–Kwong equation of state (Redlich et al., 1949). Finally, a point by point adsorptive dosing procedure detailed elsewhere (Moret et al., 2003) was used to evaluate pseudo-differential heat of adsorption noted $\Delta_{\mathrm{ads}}\dot{h}$.

3. Computational Methodology

The crystal structure of the zeolite system was modelled as follows. The purely siliceous faujasite $Si_{192}O_{384}$ with a cubic unit cell and lattice parameter of 24.8 Å was considered to represent the DAY zeolite. This assumption is a reasonable first approximation because the DAY has a Si/Al ratio of 100 which corresponds only to 1.9 Na⁺ per unit cell and no experimental data are available in the literature about the location of these extra-framework cations. The total energy of the zeolite framework and adsorbed molecules (E) is expressed as the sum of the interactions energy between the adsorbate and the zeolite (E_{AZ}), and that between the adsorbates (E_{AA}).

$$E = E_{\mathrm{AZ}} + E_{\mathrm{AA}} \qquad (2)$$

E_{AZ} and E_{AA} are both written as sums of pairwise additive potentials of the form:

$$e_{ij} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{r_{ij}} \qquad (3)$$

where the first term is the repulsion-dispersion Lennard Jones potential (LJ) with ($\varepsilon_{ij}, \sigma_{ij}$) corresponding to the parameter sets for each interacting pairs, and the second term is the coulombic contribution between point charges q_i, q_j separated by a distance r_{ij}.

The faujasite system is assumed to be semi-ionic with atoms carrying the following partial charges (in electron units): Si (+2.4 e) and O_z (−1.2 e). For nitrogen, we used the three point charge model developed by Murthy et al. (1980), where the two outer sites separated by a distance of 1.098 Å, have a charge of $q = -0.4048$ e, and the third midpoint has a point charge $-2q$. Argon is charge neutral. Moreover, R. Bell who has recently derived new interatomic potentials for the two other gases, used +0.12 e on H and −0.48 e on C for methane, and −0.36 e on O and +0.72 e on C for carbon dioxide.

Furthermore, considering that the polarizability of silicon atoms is much lower than those of oxygen atoms, the repulsion-dispersion term of the zeolite may be assigned only to oxygens of the framework. The calculation thus only requires the knowledge of the LJ parameters between the oxygens of the framework and argon, nitrogen, methane and carbon dioxide for modelling the adsorbate-adsorbant interactions. The parameters for argon and nitrogen were slightly corrected from previous studies (Mellot et al., 1997) and those for methane and carbon dioxide were deduced from the work of R. Bell who defined appropriate potential parameters by fitting potential energy surfaces for model cluster using quantum mechanical methods (Bell, 2004). The adsorbate-adsorbate LJ parameters for argon (Hirschfelder et al., 1954) and nitrogen (Murthy et al., 1980) were taken from the literature and those for methane and carbon dioxide were extracted from the work done by one of us (Bell, 2004). Table 1 summarises the various potential parameters used in this work. The Ewald summation was used for calculating electrostatic interactions and the short range interactions were calculated with a cutoff distance of 12 Å.

Table 1. Pair potential parameters used for Argon, Nitrogen, Methane, Carbon Dioxide and O_{Zeolite} in the simulation.

Interacting pairs	ε (eV)	σ (Å)	Interacting pairs	ε (eV)	σ (Å)
Argon			Nitrogen		
Ar-Ar	0.010300	3.40	N-N	0.003140	3.32
Ar-O_Z	0.012000	3.05	N-O_Z	0.006626	3.01
Methane			Carbon dioxide		
H-H	0.000660	3.19	O-O	0.006590	3.36
C-C	0.003090	3.89	C-C	0.004020	3.83
C-H	0.001357	3.70	O-C	0.001580	3.31
C-O_Z	0.004987	3.59	C-O_Z	0.003630	3.90
H-O_Z	0.003517	3.25	O-O_Z	0.006000	3.48

Absolute adsorption isotherms were computed using Grand Canonical Monte Carlo calculation algorithm which allows molecular displacements (translations and rotations), creation and destruction. These simulations consist in 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 300 K using one unit cell of faujasite with typically from 3.10^6 to 5.10^6 Monte Carlo (MC) steps. The evolution of the total energy over the MC steps was plotted in order to control the equilibrium conditions. The zeolite structure was assumed to be rigid during the sorption process. Furthermore, as it is well established experimentally and theoretically that each type of gas molecule investigated in this study can not access the sodalite cages, dummy atoms with appropriate van der Waals radius were placed in theses cages in order to avoid the introduction of adsorbate in this space. The variation of absolute differential enthalpy of adsorption as a function of the coverage was then calculated at 300 K through the fluctuations over the number of particles in the system and from fluctuations of the internal energy U as following (Nicholson et al., 1982):

$$\Delta \dot{H} = RT - \frac{\langle U.N \rangle - \langle U \rangle \langle N \rangle}{\langle N^2 \rangle - \langle \langle N \rangle \rangle^2} \qquad (4)$$

where $\langle \rangle$ corresponds to an ensemble average.

Furthemore, this fluctuation method allowed us to calculate the differential enthalpies at zero coverage $\Delta_{ads}\dot{h}_{\theta=0}$ by considering very low pressure and switching off the adsorbate-adsorbate interactions.

4. Results and Discussion

Figure 1 reports the absolute isotherms of adsorption for both non polar Fig. 1(a)) and quadrupolar gases

(Fig. 1(b)) in DAY obtained both experimentally and theoretically at 300 K. It has to be mentioned that nitrogen and argon deviate only slightly from ideal gas behaviour in the whole range of pressure up to 50 bars whereas carbon dioxide and methane show larger deviations in the same pressure range. In these latter cases, the experimental and simulated data data were corrected to take into account this non-ideal behaviour. We observe that the simulated absolute isotherms reproduce quite well the experiments for argon, methane and carbon dioxide and under-estimate the loading over 25 bars for nitrogen.

Figure 2 reports the evolution of the differential enthalpy of adsorption for both non polar (Fig. 2(a)) and quadrupolar gases (Fig. 2(b)) obtained both experimentally and theoretically at 300 K. We can observe that the adsorption of both argon, nitrogen and methane on DAY (Figs. 1(a) and 1(b)) gives within the experimental error, almost constant differential enthalpy values suggesting a balance between decreasing adsorbate-adsorbent interactions (i.e. mildly "heterogeneous" adsorbent) and increasing adsorbate-adsorbate interactions. The heterogeneity of the DAY sample comes from the residual 1.9 Na^+ extra-framework cations or from a low concentration of textural defect sites formed during the dealumination process, as was revealed by our microscopy observation, thus leading to some preferential sites for the two adsorptive gases. Finally carbon dioxide exhibits a different behaviour with an increase of the differential enthalpy when the loading increases.

Our simulation performed on a purely siliceous faujasite without any structural defects reproduces well the range of the experimental values but shows for the four gases an increase of the differential enthalpy with increasing coverage which is much more pronounced for carbon dioxide, and characteristic for gas-homogeneous surface interaction. These simulated
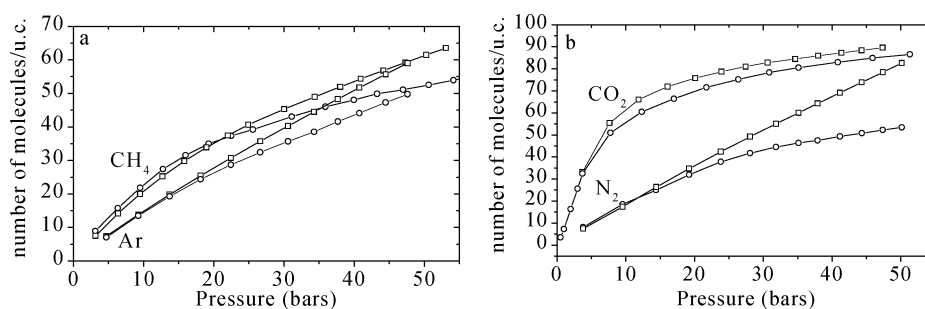

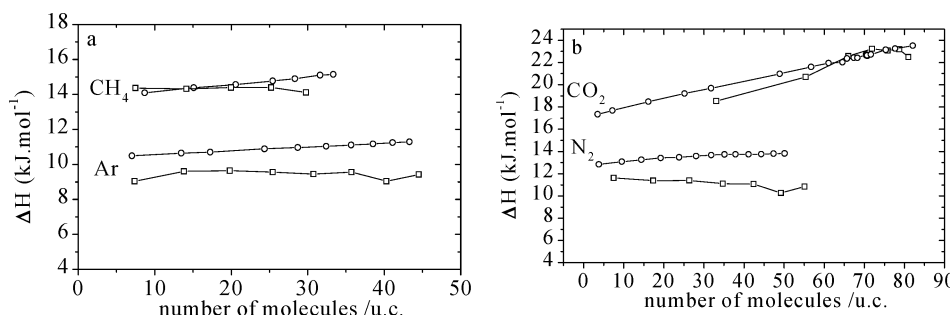*Figure 1.*   Isotherms of adsorption for (a) non polar and (b) quadrupolar gases in DAY at 300 K.

Figure 2. Evolution of the differential enthalpy of adsorption as a function of coverage for (a) non polar gases/DAY and (b) quadrupolar gases/DAY at 300 K (square: simulation, circle: experiment).

results are similar to those experimentally reported for silicalite (Dunne et al., 1996). Furthermore, the analysis of the distribution of the potential energies for adsorption of these gases proves the existence of only one type of adsorption site uniformly distributed over the supercages. We have thus shown that the much higher increase for carbon dioxide is only due to stronger lateral interactions between the adsorbates themselves. In this case, this strong adsorbate/adsorbate interaction could be predominant in DAY thus leading to an increase of the differential enthalpy of adsorption. One has to remember that some discrepancy between experiment and simulation could be due to the characteristics of the DAY sample (textural defects and presence of residual cations) not included in our computational model.

Table 2 reports the experimental and simulated differential enthalpy of adsorption at low coverage for each gas. Despite the underestimation of these values for argon and nitrogen, we reproduce the same trend as observed experimentally. It is worth noting that we find a nice agreement between experiment and simulation for methane and carbon dioxide, obtained from the new interatomic potential reported in this paper.
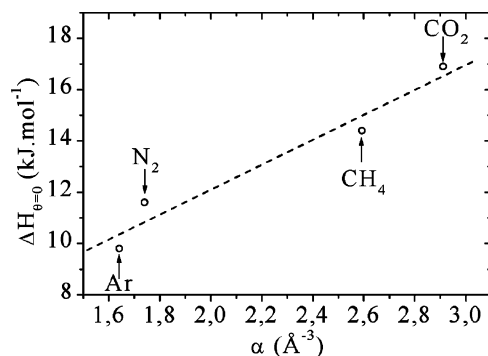

Figure 3. Evolution of the differential enthalpy of adsorption at low coverage in DAY at 300 K as a function of the polarisability of the gas molecule.

Additionally, we can observe in Fig. 3 that the differential enthalpy of adsorption at low coverage increases with the polarisability of the sorbent molecules. This behaviour indicates that for both non polar and quadrupolar gases, the predominant interaction with the zeolite framework of DAY is of dispersive type compared to the electrostatic contribution which is also pointed out in our GCMC simulations.

5. Conclusions

We have shown that the interactions of both non polar and quadrupolar gases with siliceous faujasite are mainly of a dispersive nature. It leads to an evolution of the enthalpy of adsorption at low coverage as a function of the polarisability of the gases. The new force fields derived for methane and carbon dioxide were validated in this study showing a good agreement with the macroscopic experimental data extracted from the microcalometry. It is the first time that an interatomic potential for carbon dioxide gives such nice results across

Table 2. Differential enthalpies of adsorption at low coverage in DAY at $T = 300$ K.

Type of gas	$\Delta \dot{H}_{\theta=0}$ (kJ·mol^{-1}) experiment	$\Delta \dot{H}_{\theta=0}$ (kJ·mol^{-1}) simulation
Argon	9.6	10.7
Nitrogen	11.7	12.6
Methane	14.4	13.8
Carbon dioxide	16.8	17.0

a wide range of pressure. This work represents a first step which will be followed by investigating the interactions of the same series of gases on heterogeneous ion-exchange X and Y faujasites, an opportunity to test the transferability of the new interatomic potentials. The final goal of this work in progress aims to propose a microscopic description of the adsorption phenomena in qualitative accordance with experiments and to define a simple way to predict enthalpies of adsorption on such zeolite systems from specific properties of the extra-framework cations.

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