Adsorption 11: 343–347, 2005

Nitrogen Adsorption on Divalent Cation Substituted X-Faujasites: Microcalorimetry and Monte Carlo Simulation

GUILLAUME MAURIN, PHILIP L. LLEWELLYN*, THOMAS POYET AND RENAUD DENOYEL
MADIREL, CNRS-Université de Provence (UMR 6121) Centre St. Jérôme, 13397 Marseille Cedex 20, France
pllew@up.univ-mrs.fr

Abstract. Isotherms, differential enthalpies of adsorption and Henry's constants were obtained for nitrogen at 300 K on CaX, BaX, SrX and MnX faujasite systems. The experimental data are compared with those obtained by Monte Carlo simulations based on newly derived force fields for describing the interactions between the extra-framework cations and the adsorbates. It is the first time that such good qualitative agreement is reported between experiment and simulation for a series of divalent cations.

Keywords: Microcalorimetry, Monte Carlo simulations, X-faujasite , divalent cations, nitrogen

1. Introduction

The industrial importance of zeolites not only stems from their pore structures which can be selected to suit the desired application but also to the possibility to vary the chemical composition (Froment et al., 2003). Aluminosilicate zeolites consist of networks of TO_4 tetrahedrals (T = Si or Al) linked by oxygen atoms. The substitution of silicon by aluminium atoms induces a negative charge which is counterbalanced by the introduction of monovalent or divalent extra-framework cations. In the past few years, several studies including both experiments (Salla et al., 2004) and molecular simulations (Beerdsen et al., 2003) have dealt with the influence of both the nature, distribution and 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 on the adsorption phenomena in such materials, for instance in the separation of air by pressure/vacuum swing adsorption procedures involving lithium cation exchanged faujasite zeolites as adsorbents (Fitch et al., 1995). Such processes are based on specific interactions of the adsorbents with the field gradient generated by the cations. Systematic studies were focused on the adsorption properties of X-faujasite systems containing various monovalent and divalent cations with respect to different adsorbates such as ethane and ethene (Bezus et al., 1971), water vapour (Dzhigit et al., 1971) methane (Zhang et al., 1991) or carbon dioxide (Barrer et al., 1965). They established simple relationships showing that the initial enthalpy of adsorption obtained from various methodologies including calorimetric, volumetric and virial adsorption model, usually increases with increasing charge density of the cations or with decreasing cation size.

In this work, our aim is to investigate the interactions of a quadrupolar gas (nitrogen) on a series of X-faujasites containing various divalent cations (Ca^{2+}, Ba^{2+}, Sr^{2+}, Mn^{2+}) at ambient temperature by combining microcalorimetry and molecular simulation approaches. From an experimental point of view, the calorimetric study provides a significant contribution because there is only a limited number of available data for divalent cations. From a theoretical standpoint, we have followed an original approach based on Grand Canonical Monte Carlo simulations, which consists of deriving firstly new LJ parameters for Na^+-N_2 and O-N_2 (where O corresponds to the oxygen of the zeolite framework) by fitting both the isotherm and the evolution of the differential enthalpy of adsorption for NaX/N_2 system up to 50 bars at ambient temperature.

*To whom correspondence should be addressed.

The second step consists of defining the LJ parameters for M-N_2 (M = Ca^{2+}, Ba^{2+}, Sr^{2+}, Mn^{2+}) from the Na^{+}-N_2 ones by a simple model based only on intrinsic properties of the extra-framework cations, i.e. polarisability and ionic radius. From these new interatomic potentials described elsewhere (Maurin et al., 2004), the simulation of the adsorption properties are reported in this paper including both the differential enthalpies at low coverage, isotherms and Henry's constants. These simulated data are compared and contrasted with those measured experimentally. To the authors' knowledge, it is the first time that such a good agreement between experiment and simulation is obtained for the adsorption properties involving a series of divalent cations. This accordance testifies the nice transferability of our derived force fields.

2. Experimental

2.1. Materials and Characterisation

The structure of the Faujasite type zeolite used in this investigation consists of large cavities (supercages) which have roughly spherical symmetry and diameter around 14.0 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 (Meier et al., 1978). The monovalent and divalent extra-framework cations occupy various crystallographic sites (Mortier, 1982). The various samples investigated in this work (CaX, BaX, SrX and MnX) were supplied by Air Liquide. The base material was NaX powder (Si/Al = 1) and the divalent cations forms of zeolite X were prepared by following a conventional ion-exchange technique using various aqueous salt solutions. These cation exchange treatments were repeated in order to obtain the highest degree of exchange.

The various samples were then carefully characterised. The chemical analysis were performed by using Electron Dispersive Spectroscopy (EDS) and showed that each sample is characterised by Si/Al ratio equal to 1 which means that the framework composition remained unaltered during the cation exchange process. This analysis also showed that a degree of cation exchange close to 95 and 85% was reached for (CaX, SrX) and (BaX, MnX) respectively. Powder X-ray diffraction revealed the samples to be highly crystalline and the so-obtained diffractograms showed all the characteristics peaks closely matching those predicted in the literature for Low Silica X (LSX) Faujasite system (Treacy et al., 2001). Furthermore, the morphology and the texture of each exchanged sample examined by scanning electron microscopy (SEM) remained unchanged by comparison with those observed for the parent NaX sample. Finally, the micropore volumes and surface areas of the investigated samples, determined by nitrogen adsorption at 77 K are in agreement with those reported in the literature (Zhang et al., 1991).

2.2. Microcalorimetry Measurements

Prior to each adsorption experiment, the sample is outgassed using Sample Controlled Thermal Analysis, SCTA (Rouquerol, 1989). The samples were thus heated under a constant residual vacuum pressure of 0.02 mbar up to a final temperature of 450°C which was maintained until the residual pressure was less than $5{\cdot}10^{-3}$ mbar. The adsorption at 300 K up to 1 bar was carried out by means of a Tian-Calvet type isothermal microcalorimeter built *in house*. The experiments were carried out using a high resolution quasi-equilibrium procedure of gas introduction (Grillet et al., 1977) on around 1 g of sample. This apparatus allowed us to obtain both the isotherms and the pseudo differential enthalpies of adsorption at low coverage for each X-faujasite/N_2 system.

3. Computational Methodology

The crystal structure of the X-faujasite system with the various divalent cations was modelled as follows. The chemical composition $Si_{96}Al_{96}M_{48}O_{384}$ (with M = Ca^{2+}, Mn^{2+}, Sr^{2+} and Ba^{2+}) was considered in order to reproduce the Si/Al ratio equal to 1 of the investigated samples and the framework was built with a strict ordered alternation of aluminium and silicon atoms in accordance with the Lowenstein's Al-O-Al avoidance rule (Lowenstein, 1954). We started from a diffraction refinement of the dehydrated CaX faujasite (Vitale, 1995) where the 48 Ca^{2+} extra-framework cations are distributed as follows: 16 Ca^{2+} cations in sites I located in the center of hexagonal prisms which connect the sodalite cages and 32 Ca^{2+} in sites II corresponding to the 6-ring windows of the supercages. This distribution of the extra-framework cations was also used to model in a first approximation BaX (Mellot, 1993), SrX and MnX faujasites.

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_{AZ} and E_{AA} are both written as sums of pairwise additive potentials including repulsion-dispersion Lennard Jones potential (LJ) with (ε_{ij},σ_{ij}) corresponding to the parameters sets for each interacting pairs, and 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 (expressed in electron units): Si (+2.4), Al (+1.55), O (−1.2) and M (+1.7). The effective charge of the extra-framework cations was thus reduced to take into account a partial charge transfer from the framework (Maurin et al., 2004). For nitrogen, we used the three point charge model (Murthy et al., 1980), where the two outer sites separated by a distance of 1.098 Å, have a charge of $q = -0.4048$, and the third midpoint has a point charge $-2q$. The LJ parameters corresponding to the interactions adsorbate/adsorbate $\varepsilon_{N\text{-}N}$,$\sigma_{N\text{-}N}$ were given values 0.00314 eV and 3.318 Å respectively (Murthy et al., 1980).

Furthermore, considering that the polarisabilities of silicon and aluminium atoms are much lower than those of oxygen atoms, the repulsion-dispersion term of the zeolite system may be assigned only to oxygens of the framework (O) and extra-framework cations (M). The calculation thus only requires the knowledge of the LJ parameters ($\varepsilon_{O\text{-}N}$,$\sigma_{O\text{-}N}$) and ($\varepsilon_{M\text{-}N}$,$\sigma_{M\text{-}N}$), for modelling the adsorbante-adsorbaent interactions. In this way, we have introduced the new derived parameters obtained by our previous original methodology (Maurin et al., 2004) where the ionic radii for each extra-framework cations were taken from the litterature (Huheey et al., 1993). The Ewald summation was used for calculating electrostatic interactions and the short range interactions were calculated with a cutoff distance of 12 Å.

Absolute adsorption isotherms were computed using a Grand Canonical Monte Carlo calculation algorithm. All these simulations were performed at 300 K using one unit cell of faujasite with typically from $3 \cdot 10^6$ to $5 \cdot 10^6$ Monte Carlo (MC) steps. The zeolite structure was assumed to be rigid during the sorption process. Furthermore, as it is well established experimentally and theoretically that nitrogen can not access the sodalite cages, dummy atoms with appropriate van der Waals radii were placed in theses cages in order to avoid any introduction of adsorbates in this space, thus leading to accessibility of gas only in the supercages. The calculation of the differential enthalpies of adsorption at zero coverage $\Delta_{ads}\dot{h}_{\theta=0}$ at 300 K was performed through the fluctuations over the number of particles in the system and from fluctuations of the internal energy U by considering very low pressure and switching off the adsorbate-adsorbate interactions.

Henry's constant (K_H) which is defined as the simulation cell loading divided by the pressure in the limit of vanishing pressure was evaluated for each M-X/N_2 system by the following finite sum which approximates the integral established by Bezus et al., (1978):

$$K_H = \frac{1}{N}\frac{V_{cell}}{kT}\sum_{i=1}^{N}\exp\left(-\frac{U}{kT}\right) \qquad (1)$$

where N is the number of MC steps, V_{cell} is the volume of the cell and U is the internal energy of the adsorbate molecule.

By displaying K_H as a function of the number of MC steps (N), we assess the number of MC steps about $2 \cdot 10^6$ needed to obtain a well-converged estimation of K_H.

4. Results and Discussion

Table 1 reports the experimental and simulated differential enthalpy of adsorption at low coverage for each investigated X-Faujasite. We can observe that this value increases in the order MnX > CaX > SrX > BaX. Similar behaviour has been found for methane adsorption on alkaline earth metal X systems where the sequence for isosteric enthalpy of adsorption CaX > SrX > BaX was attributed to an increase of the charge density of the cations (Zhang et al., 1991). Furthermore, the simulated values are very close to those experimentally measured for each X-system. This qualitative agreement experiment-simulation shows a nice transferability of the LJ potential parameters derived with our simplified model for each cation.

Table 1. Differential enthalpy of adsorption at low coverage for the various divalent X-faujasite/N_2 systems obtained both experimentally and theoretically at 300 K.

	Differential enthalpy of adsorption at low coverage $\Delta_{ads}\dot{h}_{\theta=0}$ (kJ·mol^{-1})	
Type of zeolite	Experiment	Simulation
MnX	30.00 ± 0.18	30.1
CaX	27.00 ± 0.16	26.5
SrX	26.00 ± 0.16	26.0
BaX	21.00 ± 0.13	20.8

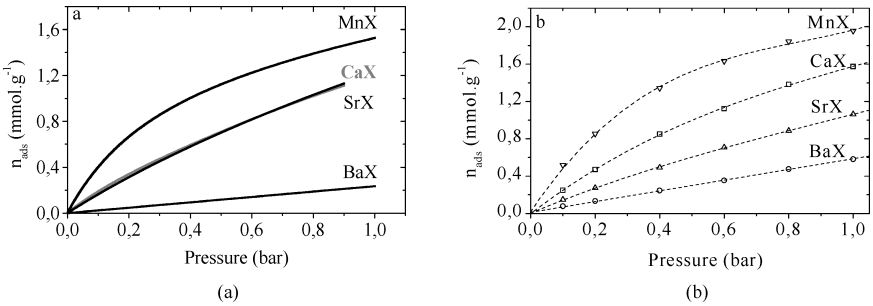

Figure 1. Isotherms of adsorption for the various divalent containing faujasites /N_2 systems at 300 K in the range of pressure [0–1] bar obtained both experimentally (a) and theoretically (b).

Figures 1(a) and (b) show the absolute isotherms of adsorption obtained for nitrogen in X-systems both experimentally and theoretically at 300 K. The simulations indicate that the capacity of adsorption in the range of pressure 0-1 bar increases in the order MnX > CaX > SrX > BaX, thus following the increase of the differential enthalpy of adsorption. We observe experimentally a similar general trend; however the adsorption capacities for CaX and SrX are close to each other. This relative discrepancy between experiment and simulation could be due to some additional volume for SrX, i.e. textural defects created during the cation exchange process or to the approximated model used in the simulation to represent the distribution of the extra-framework cations. Note however, that good agreement is obtained at low coverage (cf. Table 2). Furthermore, the simulated isotherms are slightly higher than those obtained experimentally which could be due to the same reasons than proposed above.

The next step consists of evaluating both experimentally and theoretically the Henry's constant at 300 K for each system under study. In the Henry's region, we assume a linear relation between the excess amount adsorbed and the pressure. Figure 2 reports the evolution of these excess amount adsorbed as function of pressure in the low pressure region up to 0.025 bar for each system. This is possible as there is a large number of experimental points obtained in this region due to the high resolution method of gas introduction. The Henry's constants were then directly obtained from the slopes of these isotherms. These values are summarised in Table 2 and are compared with those obtained by MC simulation. We obtain a good qualitative agreement experiment-simulation for MnX, CaX and SrX and a relative discrepancy for BaX.

Table 2. Henry's constants for the various divalent containing faujasites /N_2 systems obtained both experimentally and theoretically at 300 K.

Henry constant k_H mmol·g^{-1}·bar^{-1}		
Type of zeolite	Experiment	Simulation
MnX	4.793	4.490
CaX	2.185	2.250
SrX	1.726	1.365
BaX	0.199	0.450

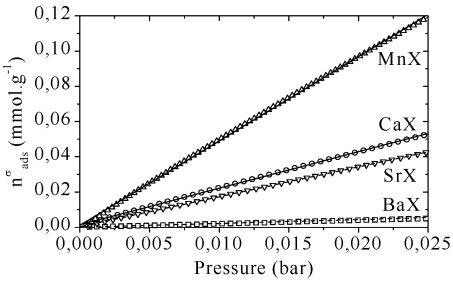

Figure 2. Isotherms of adsorption (n^{σ} excess amount adsorbed) for the various bivalent containing faujasite /N_2 systems at 300 K in the low pressure domain.

Figure 3 represents the experimental values of the differential enthalpy of adsorption as a function of the logarithm of the Henry's constant for each system investigated. These values can be correlated by means of the Van't Hoff equation (Rouquerol, 1999):

$$K_H = K_0 . \exp\left(-\frac{\Delta_{ads}\dot{h}_{\theta=0}}{RT}\right) \qquad (2)$$

where K_0 is a pre-exponential factor depending on the entropy of adsorption and the number of adsorption sites (Arik et al., 2003). From this, the slope obtained from the linear fit in Fig. 3 is 2.7 kJ · mol^{-1} which is close to the value of RT at 300 K (2.5 kJ · mol^{-1}). This observation reinforces the validity and the quality of our experiments.

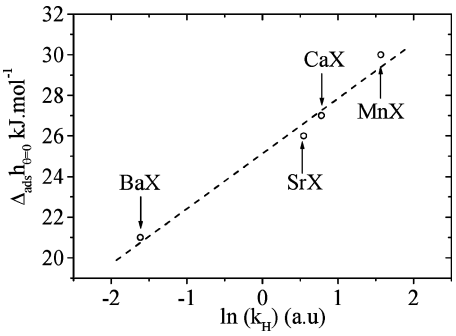

Figure 3. Linear relationship between the experimental differential enthalpy of adsorption at low coverage and the logarithm of Henry's constant for the various divalent containing faujasites/N_2 systems at 300 K.

These results suggest a similar value of K_0 for each developed divalent cation-exchanged faujasite system. It is significant as it suggests that the number of adsorption sites is the same and furthermore that the entropy of adsorption is similar.

5. Conclusions

Microcalorimetry measurements performed for nitrogen on X-faujasite systems containing divalent cations showed that the differential enthalpy of adsorption at low coverage increases in the sequence MnX > CaX > SrX > BaX. This trend was confirmed by MC simulations which gives very good qualitative accordance with the experimental values. A qualitative agreement between experiment and simulation was also obtained for the adsorption capacities and the Henry's constants. The originality of this work is the validation of the transferability of the previously derived interatomic potentials by direct comparison with our own experimental data. This work is a significant contribution as it reports for the first time such a good accordance between adsorption measurements and Monte Carlo simulations for divalent cation substituted zeolites.

References

Arik, I.C. et al., "High Temperature Adsorption of *n*-Alkanes on ZSM-5 Zeolites.: Influence of the Si/Al Ratio and the Synthesis Method on the Low-Coverage Adsorption Properties," *Micro. Meso. Mat.*, **60**, 111–124 (2003).

Barrer, R.M. and R.M. Gibbons, "Zeolitic Carbon dioxide: Energetics and Equilibria in Relation to Exchangeable Cations in Faujasite," *J.C.S., Faraday Trans. 1*, **61**, 948–961 (1965).

Beerdsen, E. et al., "Simulating the Effect of Nonframework Cations on the Adsorption of Alkanes in MFI-type Zeolites," *J. Phys. Chem. B*, **107**, 12088–12096 (2003).

Bezus, A.G., "Molecular Statistical Calculation of the Thermodynamic Adsorption Characteristics of Zeolites Using the Atom-Atom Approximation," *J.C.S., Faraday Trans.*, **74**(2), 367–379 (1978).

Bezus, A.G. et al, "Adsorption of Ethane and Ethylene on X-zeolites Containing Li^+, Na^+, K^+, Rb^+ and Cs^+ cations," *J.C.S., Faraday Trans.*, **67**(1), 468–481 (1971).

Dzhigit et al., "Heats of Adsorption of Water Vapour on X-zeolites Containing Li^+, Na^+, K^+, Rb^+ and Cs^+ Cations," *J.C.S., Faraday Trans.*, **67**(1), 458–467 (1971).

Fitch, F.R., U.S. Patent, n°5, 464, 467, 1995.

Froment, G.F. and P.A. Jacobs, "Industrial Applications of Zeolites," *Topics in Catalysis*, **13**(444), 347–357 (2000).

Grillet, Y., F. Rouquerol, and J. Rouquerol, "Study of the Physical Adsorption of Gases by a Continuous Procedure. Application to the Determination of Specific Surface Areas of Mesoporous or Non Porous Adsorbents," *J. Chim. Phys*., **7/8**, 799–782 (1977).

Huheey, J.E. *et al* "Inorganic Chemistry: Principles of Structure and Reactivity" 4th Ed., Harper Collins College Publishers, NY, 1993.

Lowenstein, W., *Am. Mineral*., **39**, 92–98 (1954).

Maurin, G. et al., "Influence of Extra-Framework Cations on the Adsorption Properties of X-Faujasite Systems: Microcalorimetry and Molecular Simulation," *J. Phys. Chem. B*, **109**, 125–129 (2005).

Treacy, M.M.J. and J.B. Higgins, *"Collection of Simulated X-ray Diffraction Powder Patters for Zeolites*," 4th revised Ed., Elsevier, Amsterdam, 2001.

Meier, W.M. and D.H. Olson, "Atlas of Zeolite Structures, *Structure Commission of the International Zeolite Association*, Elsever, Amsterdam, 1978.

Mellot, C., Ph. D. Thesis, Université de Paris VI, France, 1993.

Mortier, W.J., "*Compilation of Extraframework Sites in Zeolites*," Butterworth, Guildford, 1982.

Murthy, C.S., et al, "Pairwise Additive Effective Potentials for Nitrogen," *Mol. Phys*., **41**, 1387–1399 (1980).

Rouquerol J., "Controlled Transformation Rate Thermal Analysis: The Hidden Face of Thermal Analysis," *Thermochim. Acta*, **144**, 209–24 (1989).

Rouquerol, F., J. Rouquerol, and K. Sing, *Adsorption by Powders and Porous Solids*, Acad. Press, London, 1999.

Salla, I., "Study of the Influence of Several Mordenite Modifications on Its N_2 and O_2 Adsorption Properties," *J. Phys. Chem. B*, **108**, 5359–5364 (2004).

Sorensen, T.O. and J. Rouquerol, *Sample Controlled Thermal Analysis*, Kluwer, Dordrecht 2003.

Vitale, G. et al, "Combining Neutron and X-Ray Powder Diffraction Study of Zeolite CaLSX and H_2 NMR Study of Its Complex with Benzene," *J. Phys. Chem. B*, **99**, 16087–16094 (1995).

Zhang, S.Y., et al, "High Pressure Adsorption of Methane in NaX, MgX, CaX, SrX and BaX," *J. Phys. Chem. B*, **95**, 1722–1726 1991.