Quantum Chemical Study of Low-pressure Adsorption in Zeolitic Materials

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Zeolites are mainly used as heterogeneous catalysts, with an increasing use as gas-separation adsorbents. Their properties as adsorbents are described by adsorption isotherms and isosteric heats of adsorption. Two methods are presented that predict isosteric heats of adsorption of gaseous molecules at low coverages. Both methods are based on the quantum mechanical (QM) evaluation of the interaction between the molecule adsorbed and the cationic site treated as an embedded cation. The first method uses Boltzmann statistics, whereas the other method assumes that adsorption at low pressure can be described with a Langmuir model. These two procedures yield very comparable isosteric heats for N_2 and O_2 in Ca-A and Ca-LSX. Their comparison allows us to underline the strong heterogeneity of N_2 adsorption in Ca-LSX and the effect of temperature on the equilibrium constant of adsorption.

1. Introduction

Zeolitic materials are widely used as adsorbents. Their adsorption properties are determined by their structure, essentially their pore size and the number and location of their extraframework cations. Certain zeolites, particularly those containing Li^+ and Ca^{2+} cations, are known to have a much larger affinity for N_2 than for the other components of air. These properties are exploited in the industrial process of air separation by pressure adsorption (PSA), which involves adsorption and desorption cycles yielding a gas containing 95% oxygen.[1]

The adsorption properties of a zeolitic adsorbent with respect to a particular adsorbate are described, at equilibrium, by its adsorption isotherm, i.e., the amount of molecules adsorbed as a function of pressure, at a given temperature. The energetics of adsorption is described by the isosteric heat of adsorption, which can be estimated with different experimental techniques. Among them, the most accurate method is calorimetry, but available data are still restricted to few zeolites.[2,3] Isosteric heats can also be determined from experimental isotherms measured at different temperatures, applying the van't Hoff equation. The isosteric heat at the limit of zero coverage can be obtained from the limiting slope of an adsorption isotherm at low pressure. These techniques are very sensitive to numerical errors of differentiation and extrapolation, which leads to poor agreement between available experimental data.[4,7]

The interpretation of adsorption isotherms necessitates the use of explicit equations derived from the thermodynamics description of mixtures and from statistical thermodynamics. However, it must be stressed that the choice of a theory of adsorption is the underlying requirement to any interpretation and/or prediction of adsorption isotherms.[8] Extensive work has provided analytical equations able to predict isotherms with the necessary introduction of surface heterogeneity.[9] Generally, the description of adsorption is based on the concept that the adsorption on the heterogeneous surface can be described as a summation over various parts, sites, or patches, each part being treated as a local homogeneous adsorbent (with a given adsorption energy).

The most common model for a local adsorption isotherm is the one proposed originally by Langmuir.[10] Many other equations have been proposed afterward, to improve the prediction of single-component and multicomponent adsorption equilibria.[11,12] The energy function is generally obtained as a parameter, after fitting the theoretical expression against the experimental isotherm or using calculated interaction energies.[13–16] The reliability of these methods lies essentially in the quality of the interaction potentials, whereas their major difficulty lies in the transferability of adjusted parameters.

We have shown previously that all qualitative trends of N_2/O_2 separation in various zeolitic frameworks can be described by a quantum mechanical (QM) description of the couple cation–adsorbate, embedded in the environment of the zeolite, which is treated as in molecular mechanics (MM) and interacts electrostatically with the QM system.[17,18] In particular, this approach has underlined the heterogeneity of LSX zeolites, its dependence on the nature and positions of the extraframework cations and also on the nature of the adsorbate.[19] Adsorption can occur at many different sites within cages and channels. In this study devoted to low-coverage adsorption, we will neglect all other sites than cations, which, in any case, are always the most favored sites. In Ca-LSX and Ca-A, the only accessible cations are located in the supercages.

The novelty of the present approach is that, based on QM/MM calculations of the adsorption energies at the various adsorption sites, i.e., taking into account all kind of adsorbent–adsorbate interactions without adjusting parameters, we show that it is possible to estimate the isosteric heats of adsorption, assuming that the adsorbate molecules are in a gaseous state. On this basis, we have found it interesting to compare two approaches: (i) estimating the isosteric heats of adsorption at zero coverage of N_2 and O_2 in Ca-LSX and Ca-A, based on the

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QM/MM adsorption energies of a single adsorbate molecule, and (ii) predicting Langmuir isotherms at low pressures for several temperatures and estimating the isosteric heats of adsorption, by use of the van't Hoff equation. The comparison of the two methods gives some insight into the physical significance of these quantities.

2. Thermodynamics Relations

The adsorption of gaseous molecules in zeolites is a dynamical equilibrium between adsorption and desorption on the surface:

$$M \text{ (gas)} + S \text{(surface)} \leftrightarrow MS \text{ (adsorbed state)}$$
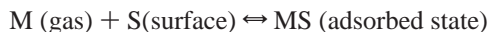
In this approach, we will consider that the adsorption occurs at localized sites, i.e., the accessible extraframework cations. The interaction energy of an isolated molecule is described by its potential energy $E(r)$, r being its distance from the cation.

The equilibrium constant K can be expressed by use of the relation between K and the Gibbs energy of reaction:[20]

$$K = \frac{q_m(MS)}{q_m(M)} e^{-\Delta E_0/RT} \tag{1}$$

The variables $q_m(MS)$ and $q_m(M)$ are the standard molar partition functions of the adsorbed and free molecules, respectively. ΔE_0 is the difference in molar energies of the adsorbed and gaseous species. The q_m and ΔE_0 values, which are characteristics of the interaction between the zeolite and a gaseous molecule, can be evaluated theoretically, leading to an estimate of the equilibrium constant K.

The prediction of isotherms and isosteric heats of adsorption requires, in addition, a model for adsorption, i.e., a function relating the pressure to surface coverage. The simplest theoretical model for monolayer adsorption is due to Langmuir:[10]

$$\theta = \frac{n}{n_m} = \frac{Kp}{1 + Kp} \tag{2}$$

where θ is the surface coverage, n is the number of molecules adsorbed at the pressure p, and n_m is the saturation number.

The model is based on three assumptions: (i) there is only one layer of adsorbate molecules, (ii) there is no interaction between molecules adsorbed at different sites, and (iii) all sites are equivalent, i.e., the surface is homogeneous.

Given these limitations, the Langmuir formula is used generally to estimate the isosteric heat of adsorption from experimental isotherms, by use of the van't Hoff derivation:

$$\left[\frac{\partial \ln p}{\partial(1/T)}\right]_n = -\left[\frac{\partial \ln K}{\partial(1/T)}\right]_n = \frac{\Delta H_{ad}}{R} = -\frac{q_{st}}{R} \tag{3}$$

where q_{st} is the isosteric heat of adsorption for a given number n of adsorbed molecules.

In reality, the adsorption enthalpy varies with the temperature, but this variation is assumed to be small in a given range of temperatures and eq 3 can thus be applied to calculate q_{st} from isotherms measured within this range of temperatures, as the slope of the linear relation between $\ln K$ and $1/T$. Moreover, according to the ideal Langmuir model defined above, the isosteric heat of adsorption must be independent of coverage (no adsorbate−adsorbate interaction, homogeneous surface). The homogeneity of the surface, on which the method is based, can be estimated from the values obtained for q_{st} at different coverages of the surface. In fact, the most direct experimental

evidence of the heterogeneity of adsorption is the decrease of q_{st} with increasing n values.[11]

The limiting slope of an experimental adsorption isotherm at zero pressure (Henry's constant) characterizes the adsorpion of one molecule at the surface. Its dependence with temperature yields the isosteric heat of adsorption at zero coverage q_{st}^0.

Since we are interested, in this study, to predict isosteric heats of adsorption at zero coverage, the Langmuir isotherm, restricted to low pressures should be sufficiently accurate.

3. Methodology

3.1. Ca-LSX and Ca-A Structures. Ideal dehydrated Ca-LSX and Ca-A zeolites (Si/Al = 1) contain 48 calcium cations/unit cell. Whereas the LTA structure accommodates 6 cations per sodalite cage, located in the middle of six-membered rings, the LSX zeolite has only 32 possible calcium ions in six-membered rings (sites II), the remaining 16 cations being distributed in sites I and I′.

A recent experimental structure has been chosen for Ca-LSX, which includes indeed 32 site II Ca cations, the remaining 16 cations being distributed in 12 sites I and 4 sites I′.[21] The repartition of these 16 cations has been obtained with minimization of their mutual repulsion. Since no recent Ca-A structure with a Si/Al ratio close to 1 was available in the literature, this structure has been generated by MM simulation, by use of the aluminosilicate cvff_aug force field within Cerius2.[22] The obtained average bond lengths and angles are 1.61 Å, 1.79 Å, and 149.8° for Si−O, Al−O, and Si−O−Al, respectively. There are three short (2.35 Å) and three long (3.25 Å) Ca−O bond distances in the six-membered rings.

3.2. Adsorption Energies from QM/MM Calculations. Previous work has shown that a QM/MM method is suitable for studying adsorption of gaseous molecules in zeolitic frameworks.[17−19] The strategy adopted in this methodology is to model adsorption of N_2 or O_2, in turn, at each accessible cation in one crystal unit cell, i.e., 32 and 48 calcium cations in ideal Ca-LSX and Ca-A, respectively (Si/Al ratio equal to 1).

The embedded cluster consists of a Ca^{2+}−molecule (N_2 or O_2) system treated quantum chemically, surrounded by the specific environment of each cationic site, i.e., point charges simulating the Al, Si, O, and Ca^{2+} zeolite ions. This methodology allows us to take account for long-range effects, which may differ from one cation to another in the LSX structures.[18]

The QM calculations have been performed within the framework of density functional theory with the deMon program.[23,24] Gradient-corrected potential and energy functionals have been used for exchange[25] and correlation.[26] All technical details are described in ref 17.

As discussed in ref 19, this method implies to choose the values of the charges representing the zeolite atoms. At first sight, this is not a trivial problem, since charges are not directly measurable properties. The embedding charges used in this study, i.e., Si (+2.4), Al (+1.4), O (−1.2), and Ca (+2.0), are those used for MM simulations.[18] The QM calcium cations were also assumed to bear a +2 charge, i.e., neglecting any zeolite to cation charge transfer (CT). Previous studies on Li-LSX (containing site II and site III accessible cations) and Ca-LSX have shown that there is a negligible effect of the embedding charge values on adsorption energies at sites III (≤0.2 kcal/mol), whereas this effect is larger at sites II, due to larger local electric field components.[19] The tendency is an increase of adsorption energies with a decrease of the embedding charges (absolute values): for Ca-LSX, the adsorption energies of the

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"best" cations are increased by 0.9 kcal/mol, when the set of charge mentioned above is replaced by a Mulliken-type set (Si +1.6; Al +0.6; O −0.8; Ca +2.0). The "best" cations are those involved in the estimation of the isosteric heats of adsorption at low coverage. This relatively small influence of the embedding charges is due to a balance between all positive and negative contributions, because the electric field value at one point of the studied unit cell is converged (large enough embedding).

On the other hand, taking into account the zeolite to cation CT decreases the calcium positive charge and, consequently, decreases the adsorption energies.[19] If this CT is included in the QM calculation, populating the 4s Ca orbital with a fractional number of electron, the "best" sites of Ca-LSX have decreased adsorption energies: this decrease amounts to 0.6 kcal/mol for a CT of 0.3 electron (value obtained from QM calculations of zeolite cluster models)

The error due to these two effects being of opposite sign, we think that the isosteric heats reported here, using the given set of embedding charges and neglecting the zeolite to calcium CT, are estimated with an error smaller than 0.5 kcal/mol, which is acceptable for a comparison with experimental heats of adsorption.

Our previous studies have shown that adsorption heterogeneity is lower in Ca-LSX than in Li- or Na-LSX, due to the lack of site III cations, which introduce a large dissymmetry in the structure. The moderate spread of adsorption energies (4 kcal/mol) is due to the nonsymmetric distribution of site I/I′ cations. Ca-A has an even more symmetric framework with no site I/I′ cations and eight similar supercages, which implies a very weak heterogeneity of adsorption sites.

3.3. Isosteric Heats at Zero Coverage from QM/MM Calculations. At very low coverage, there are as many possible adsorption sites as cations for each adsorbate molecule. However, according to statistical thermodynamics, there is a dominating configuration for which the populations of the adsorption sites are defined by the Boltzmann distribution. The enthalpy of adsorption at T can thus be expressed as

$$\Delta H(T) = \sum_i \Delta H_i p_i \qquad (4)$$

with

$$p_i = \frac{\exp(-\Delta H_i/RT)}{\sum_i \exp(-\Delta H_i/RT)} \qquad 0 \leq p_i \leq 1$$

The ΔH_i are the calculated adsorption enthalpies at each cationic site, i.e., the QM/MM adsorption energies corrected for zero-point, thermal effect of vibrational levels, and change from internal energy.

$\Delta H(T)$ represents the enthalpy of adsorption of the first molecule adsorbed. When more molecules are introduced in the zeolite, the adsorption sites are occupied according to various configurations. They lead to a comparable heat of adsorption if the individual enthalpies of adsorption are similar (neglecting adsorbate−adsorbate interactions) and to decreasing heats of adsorption if they are very different, i.e., if the adsorption is heterogeneous.

$\Delta H(T)$ should thus be a good estimate of the isosteric heat of adsorption at the limit of zero coverage, at the temperature T.

3.4. Calculated Isotherms. Another way to evaluate isosteric heats of adsorption is to follow the same procedure as used to estimate them from experimental isotherms but, instead, to use theoretical Langmuir isotherms calculated with theoretical K values.

However, to take the heterogeneity of adsorption sites into account, the surface can be modeled as a sum of patches, i.e., the cationic sites, each one being described with a Langmuir isotherm. This method, also called the multisite Langmuir model, allows us to express the global surface coverage as a sum of individual contributions:

$$\theta = \frac{n}{n_m} = \sum_i \frac{K_i p}{1 + K_i p} \qquad (5)$$

where i represents each cationic site and n_m is the number of cations per unit cell, i.e., 32 for Ca-LSX and 48 for Ca-A. The number n of molecules adsorbed per unit cell is thus expressed as a sum over all available cations. By use of eq 1, each local equilibrium constant is evaluated as

$$K_i = b_i \exp\frac{(-\Delta E_{0i})}{RT} \qquad \text{with} \qquad b_i = \frac{q_{m,i}(MS)}{q_m(M)} \qquad (6)$$

Each $q_{m,i}(MS)$ is the local molar partition function at each cationic site for the adsorbed system, whereas $q_m(M)$ describes the gaseous state. The $q_m(M)$ values are calculated as the products of translational, rotational, vibrational, and electronic partition functions. When the molecule (atom) is adsorbed, all degrees of freedom are transformed into vibrational modes, and, eventually, frustrated movements. These various contributions to $q_{m,i}(MS)$ and $q_m(M)$ are evaluated quantum chemically, assuming that the rigid rotator and harmonic oscillator approximations are valid.[27] Of course, the thermodynamical functions $q_{m,i}(MS)$ and $q_m(M)$ depend explicitly on the temperature[28] and their ratio is thus temperature-dependent.

The K_i values are the individual equilibrium constants associated with every local isotherm, assuming each adsorption site be independent of the others. These variables depend explicitly on the temperature and the adsorption strength of the site. If all sites are equivalent, the surface is homogeneous and adsorption can be described with eq 2, where the global equilibrium constant K is equal to each equivalent K_i. When the surface is heterogeneous, K is a complex function involving pressure and the individual K_i. To estimate the global equilibrium constant K and then the isosteric heats of adsorption, we have chosen the following approach: (i) the surface adsorption is modeled with a multisite Langmuir model (eq 5), and (ii) the resulting isotherm is assumed to be equivalent to an "effective" monosite isotherm describing the whole surface, with an effective equilibrium constant K_{eff}:

$$\theta' = \frac{n'}{n_m} = \frac{K_{eff} p}{1 + K_{eff} p} \qquad (7)$$

This is achieved by fitting the multisite isotherms calculated at different temperatures with eq 7, providing the effective constants $K_{eff}(T)$. As mentioned above, ΔH_{ad} (q_{st}) and K vary with T, but choosing an appropriate ΔT allows the plot of ln $K_{eff}(T)$ against $1/T$ to be linear, yielding the isosteric heat of adsorption in this domain. The accuracy of the calculated q_{st} values is dependent on the validity of the fit yielding the "effective" constants. Therefore, only domains of temperatures

TABLE 1: Maximum and Minimum Energies of Adsorption Calculated for the Accessible Cations of Ca-LSX and Ca-A

adsorbate	Ca-LSX[a]	Ca-A[a]
N_2	−11.1; −7.5	−8.5; −7.2
O_2	−6.6; −3.4	−3.9; −2.8

[a] Energies are given in kilocalories per mole.

where the real system behaves physically as a monosite surface can be used to evaluate the isosteric heats of adsorption.

Since the assumptions inherent to the Langmuir model are less critical at low coverage, our calculated values should be a good estimate of the isosteric heats of adsorption at zero coverage.

It is worth noting that the two methods (sections 3.3 and 3.4) used to calculate the q_{st}^0 values take into account their dependence on temperature. In the first method, it appears in the terms correcting the calculated adsorption energies into $\Delta H_{ad}(T)$ and in the Boltzmann populations; in the second method, both b_i and the exponential terms depend on T, and thus also K_{eff}.

This treatment must indeed be consistent with the thermodynamics expression for the enthalpy at temperature T:

$$H(T) - E_0 = RT^2\frac{\partial \ln q_m}{\partial T} + RT \qquad (8)$$

which leads, for adsorption, to

$$q_{st} = -\Delta H_{ad}(T) = -\Delta E_0 - RT^2\left[\frac{\partial \ln q_m(MS)}{\partial T} - \frac{\partial \ln q_m(M)}{\partial T}\right] \qquad (9)$$

or

$$= -\Delta E_0 - R\frac{\partial \ln [q_m(MS)/q_m(M)]}{\partial (1/T)} \qquad (10)$$

In the temperature range ΔT, where $\Delta H_{ad}(T)$ is assumed to be constant, the logarithmic term of eq 10 must thus be constant within a good approximation (see section 4). This term is, however, not constant for all temperatures and, a fortiori, not negligible as it was assumed in previous calculations of Henry constants in a zeolite model.[29] As evidenced in eq 9, this term reflects the different response of the adsorbed molecule to temperature changes, with respect to the gaseous molecule. It is clear that an increase of temperature will affect differently the vibrational states of the adsorbed species and the degrees of freedom of the isolated system, more particularly in the case of strong adsorption. At sufficiently high temperatures, the adsorbed and gaseous states become less different and this term may then be assumed to be constant.

4. Results and Discussion

The N_2 and O_2 adsorption energies have been calculated at all the accessible sites (per unit cell) of Ca-LSX and Ca-A, i.e., 32 and 48 site II cations, respectively. The spread of these energies, as presented in Table 1, is roughly three times larger for Ca-LSX than for Ca-A, due to the nonsymmetric distribution of the 16 nonaccessible site I/I′ cations.

Adsorption in Ca-A is thus more homogeneous, leading to a more valid use of a Langmuir isotherm. It is worth noting that heterogeneity is not a property of the surface alone, since it is also dependent on the nature of the adsorbent. The same surface is more homogeneous for O_2 than for N_2 adsorption.

TABLE 2: Calculated and Experimental Heats of Adsorption for Ca-LSX and Ca-A

method	Ca-LSX[a]		Ca-A[a]	
	N_2[b]	O_2[c]	N_2[c]	O_2[c]
statistical enthalpies	9.6	5.1	7.0	2.8
enthalpies from isotherms	9.0	5.1	7.1	3.0
experiment	9.0[d]	6.7[d]	6.7[d]; 7.5[e]	5.0[d]; 3.4[e]; 3.3[f]

[a] Energies are given in kilocalories per mole. [b] Calculated at 340 K (see text). [c] Calculated at 300 K. [d] From ref 30. [e] From ref 31. [f] From ref 33.
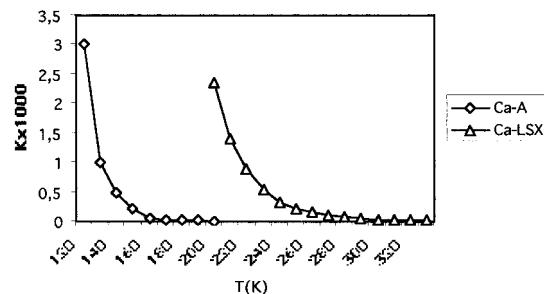
Figure 1. Variation with T of $K_{eff}(T)$ for N_2 adsorption in Ca-A and Ca-LSX.
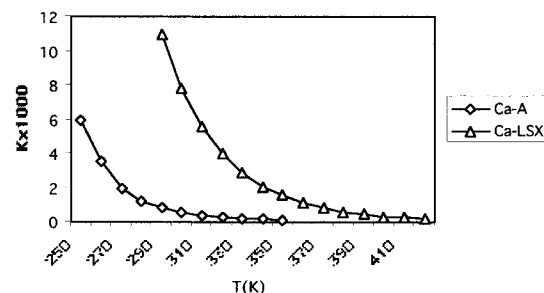
Figure 2. Variation with T of $K_{eff}(T)$ for O_2 adsorption in Ca-A and Ca-LSX.

The isosteric heats of adsorption of these gases estimated as statistical enthalpies (section 3.3) and from isotherms at different temperatures (section 3.4) are presented in Table 2. As explained below, the second set of values is valid for a range of temperatures of around 40−50 K including 300 K, except for N_2 in Ca-LSX, for which the domain of validity is shifted toward 360 K. The calculated values are compared with available experimental data. Unfortunately, there are no calorimetric measurements for these gases in Ca-LSX and Ca-A at room temperature. The experimental values reported have been derived from slopes of van't Hoff plots using Henry constants from chromatographic[30] and volumetric[31] measurements. The plot of ln K with respect to $1/T$ can be easily fitted with a linear function but the error done by use of a linear regression over a range of 70−90 K can easily reach 1 kcal mol^{-1}, according to the system. This precision being kept in mind, comparison of calculated and experimental results shows a good agreement for N_2 adsorption. The agreement is not so good for O_2, with heats of adsorption derived from chromatographic experiments, whereas our results are within the acceptable range of error in Ca-A with respect to the experimental results reported in refs 31 and 32.

To illustrate the effect of temperature on the adsorption equilibrium, the calculated K_{eff} values in Ca-A and Ca-X are drawn as a function of temperature in Figure 1 for N_2 and in Figure 2 for O_2. The range of temperatures displayed in Figure 2 has been chosen to facilitate the comparison with the values of K_{eff} for N_2 adsorption. The examination of these figures leads
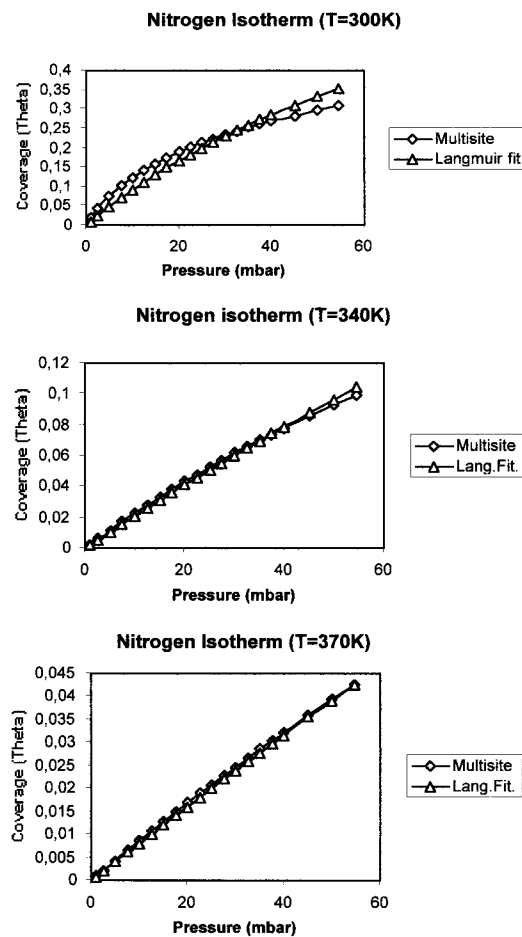
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Nitrogen Isotherm (T=300K)

Nitrogen isotherm (T=340K)

Nitrogen Isotherm (T=370K)

Figure 3. Langmuir multisite and fitted monosite isotherms for N_2 adsorption in Ca-LSX at 300, 340, and 370 K.

to three remarks that can be related to the adsorption properties of the two zeolites: (i) equivalent K_{eff} values are found at much lower temperatures for Ca-A than for Ca-LSX, because of the lower adsorption strength of the cations in Ca-A; (ii) the equilibrium constants decrease exponentially with increasing temperature, and this decrease is much steeper for Ca-A than for Ca-X, due to its larger homogeneity which makes every adsorption site behave in a comparable way; and (iii) after a steep descent, the rate of decrease of $K_{eff}(T)$ slows down by 1 order of magnitude and the function tends smoothly to very low values (and to zero). The temperature for which K_{eff} becomes less than 10^{-3} is lower for Ca-A than for Ca-X and lower for O_2 than for N_2. This property is again related with the larger adsorption strength and heterogeneity of Ca-LSX and the stronger interaction of N_2 with cations.

The change of regime in the decrease of K_{eff} occurs more clearly for values lower than around 0.001 bar^{-1}. In fact, the domain of temperatures for which the slower regime has been reached corresponds also to the domain where the fit of the Langmuir multisite curves with effective monosite isotherms yields valid results. Figure 3 shows the multisite and fitted isotherms for N_2 in Ca-LSX going from $T = 300$ to 340 and 370 K: before 350 K, there is no valid "effective" monosite surface and the related K_{eff} values have no physical significance.

The lower limit of temperature for obtaining a valid effective equilibrium constant is much lower for O_2 than for N_2 and for Ca-A than for Ca-LSX. In this context, isosteric heats of adsorption can be evaluated at 300 K for O_2 in both zeolites and for N_2 in Ca-A, whereas this method yields only a value of
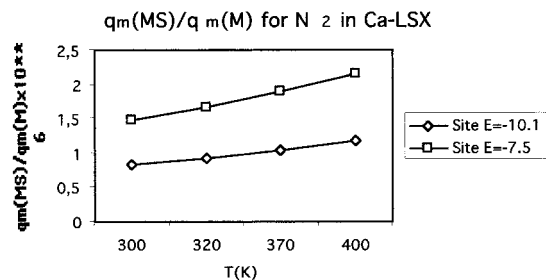

Figure 4. Variation with T of the preexponential factor $q_m(MS)/q_m(M)$ for N_2 at the highest and lowest adsorption energy sites of Ca-LSX.

q_{st} at 360 K for N_2 in Ca-LSX. In all cases a ΔT range of 40 K has been used for the linear regression of van't Hoff plots.

Comparison of the calculated q_{st} values of Table 2 shows that our two approaches give equivalent results. The statistical approach has the advantage, with respect to the global approach using effective equilibrium constants, of having no need to choose a model for adsorption. The isosteric heats calculated at various temperatures obey the Boltzmann statistics, i.e., decrease with increasing temperature, because of the population of lower energy sites. It is therefore more appropriate for the calculation of isosteric heats of adsorption at very low coverage. On the other hand, it does not provide an estimate of equilibrium constants and cannot be used for modeling adsorption of several molecules. The limitation of the second method is illustrated by the impossibility of providing a value for the isosteric heat of N_2 in Ca-LSX at 300K. This value can be predicted to be slightly larger than 9 kcal mol^{-1}, obtained at 360 K, i.e., very close to the value given by the first method. Its interest is also to underline the importance of heterogeneity for N_2 adsorption.

Finally, we have found it interesting to analyze how the preexponential factor $q_m(MS)/q_m(M)$ (eq 1) varies with temperature, since it governs the dependence of q_{st} on temperature. To illustrate also the relation of this factor to the adsorption sites, its values for N_2 have been calculated at four temperatures for the highest and lowest energy sites of Ca-LSX (Figure 4). The variation of this quantity with temperature is found to be linear, which means that $\partial \ln [q_m(MS)/q_m(M)]/\partial T$ is a constant in this domain of temperatures, justifying the use of the van't Hoff derivation to obtain q_{st}. However, the presence of sites of different adsorption strengths introduces some complexity, because the variation with T has a larger slope for weaker adsorption, as shown in Figure 4.

5. Conclusions

We have presented two methods to evaluate isosteric heats of adsorption of gaseous molecules in zeolites at low coverages, i.e., at low pressure of gas. Both methods are based on the QM description of the interaction between the molecule and the cationic site modeled as an embedded cation. The calculation of a statistical enthalpy of adsorption yields a quite accurate estimate for one single molecule in a cage, at any desired temperature. The simulation at increasing pressure would require time-consuming Monte Carlo estimates based on QM interaction energies.

On the other hand, the procedure based on the evaluation of Langmuir isotherms is limited to the domain of temperatures for which the system can be physically described as equivalent to a monosite. Its advantage is then to provide values for the equilibrium constants as well as a global description of the surface.

Since we do not use empirical parameters, this application of the Langmuir model is based on a simple statistical

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thermodynamics derivation of the Langmuir isotherm. This allows us to retain the physical significance of the thermodynamics quantities involved in the adsorption equilibrium and to clarify the definition of the isosteric heat of adsorption, which should not be confused with the adsorption energy used in eq 6. Most of the models used to interpret adsorption isotherms are based on site equilibrium constants (eq 6), where b_i and ΔE_i are parameters adjusted to reproduce experimental isotherms.[9,32] The b_i terms, often called affinity parameters, are generally considered to be independent of T and ΔE[32,33] or their dependence on T is parametrized to take account for the surface heterogeneity.[11]

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