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Do the Differential Enthalpies of Adsorption Vary Between 77 K and 302 K? An Experimental Case Study of Argon and Nitrogen on Two Faujasite Type Zeolites

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

Abstract. Adsorption microcalorimetry of non-polar argon and quadrupolar nitrogen gases was carried out at 77 K and 302 K on two chemically different faujasite type zeolites (DAY and NaX). Considering absolute quantities adsorbed, the differential enthalpies of adsorption at zero coverage obtained with each system do not vary with temperature. Similarities in the differential enthalpies with increasing coverage are observed only if one considers non-specific adsorption phenomena either with a non-polar probe or on a non-polar surface. Where "specific" polar interactions occur for the nitrogen-NaX system, significant differences are observed. This experimental study is the first to compare microcalorimetric measurements of adsorption in such a wide range of temperature.

Keywords: microcalorimetry, nitrogen, argon, faujasite, differential enthalpy, adsorption isotherm

Introduction

From several points of view it can be of interest to compare adsorption systems at different temperatures. Indeed, the isosteric method (Shen and Bülow, 1998; Bülow et al., 2002) is based on the measurement of isosteres which can then be converted to give enthalpies of adsorption as a function of adsorbate loading. More generally, one can compare a limited number of adsorption isotherms obtained within a small interval of temperature (Rouquerol et al., 1999) to obtain isosteric enthalpies of adsorption, via the Clausius Clapeyron equation. In these cases, one considers that the adsorption is reversible, i.e. that no chemisorption mechanism is involved. It is for this reason that isosteric enthalpies are obtained with isotherms measured generally within a 30 K range.

A second approach that uses the comparison of adsorption at different temperatures is the characteristic curve of Polyani (Polyani, 1920). Here one relates the relative pressure of adsorption at a given temperature to the "adsorption potential" A. Several studies have shown the validity of such an approach (Dubinin, 1966; Cartraud, 1967) for various different temperatures. Furthermore in the case of various zeolite samples, where one takes into account the cavity size, it was possible to obtain a single characteristic curve independent of temperature, adsorbate species and zeolite type (Hayhurst and Lee, 1988). The use of such a characteristic curve, implicitly assumes that the same adsorption processes occur in the whole temperature domain under investigation. This would also suggest that the interactions (adsorbate-adsorbent at low coverage and adsorbate-adsorbate co-operative effects at higher coverage), and thus the adsorption enthalpies measured, should vary with temperature.

Many adsorption studies have been carried out over wide ranges of temperature using methods such as the isosteric method (Shen and Bülow, 1998; Bülow et al., 2002), gas chromatography (Aristov and Kiselev, 1967; Aristov et al., 1967) and others. However, none of these studies has made use of direct calorimetric measurements to test the validity of the thermodynamic interpretation of results. The present study uses two

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*To whom correspondence should be addressed.

microcalorimeters that operate at 77 K and at 302 K to compare the enthalpies of adsorption on the same systems.

Model systems have been selected to allow a fundamental study of the adsorption phenomena. The adsorption of two simple gases (nitrogen and argon) is measured on two Faujasite type zeolites (same structure type) of different chemical composition. This study highlights the effects on the enthalpies of adsorption of three parameters: temperature of adsorption and chemical nature of adsorbent surface and adsorbate species.

Experimental

The nitrogen and argon were obtained from Air Liquide (Alphagaz, France) and are of purity 99.995%.

Two zeolites were chosen of the same structure type but of different chemical compositions. The Faujasite structure type is built of a three-dimensional channel network of large spherical geometry cavities (supercages with diameter of 1.4 nm) connected via windows ($d = 0.74$ nm) (Baerlocher et al., 2001). The NaX sample (Prolabo) is characterised by a Si/Al ratio of 1.0. In this structure, the negative charge of the framework induced by the introduction of aluminium is counterbalanced by extra-framework sodium cations. These cations can be considered as specific adsorption sites. DAY is the highly siliceous form of Faujasite (Si/Al = 100). It is obtained by steaming and post treatment of NaX. The framework is essentially electrically neutral although some residual cations are found in the inaccessible sodalite cages. Textural defects in the structure are formed however.

Prior to each adsorption experiment, the sample is outgassed using Sample Controlled Thermal Analysis, SCTA (Rouquerol, 1989; Sorensen and Rouquerol, 2003). Here, the sample was heated under a constant residual vacuum pressure of 0.02 mbar up to a final temperature of 450°C for 16 hours.

The differential enthalpies of adsorption were obtained directly using a Tian-Calvet type microcalorimeter (Rouquerol, 1971) coupled to a manometric apparatus (Grillet et al., 1977) built in house. Around 50 mg of sample is placed in the microcalorimeter which is itself kept in a liquid nitrogen cryostat. A quasi-equilibrium system of gas introduction allows the determination of the adsorption isotherms and the corresponding microcalorimetric recording with a high resolution.

The adsorption up to 50 bars was carried out by means of a Tian-Calvet type isothermal microcalorimeter built *in house* and recently adapted for measurements up to a pressure of 50 bars (Poyet, 2002). The experiments were carried out at 302 K with a standard point by point adsorbate dosing procedure on around 1 g of sample.

Results and Discussion

Adsorption at 77 K

Figure 1 shows the differential enthalpies of adsorption as a function of relative coverage obtained during the adsorption at 77 K of argon and nitrogen on DAY and NaX zeolite samples. In this figure and in Fig. 2, excess adsorbed quantities were used to represent the enthalpy curves. The relative coverage is calculated as the ratio of amount adsorbed to the amount required to fill the

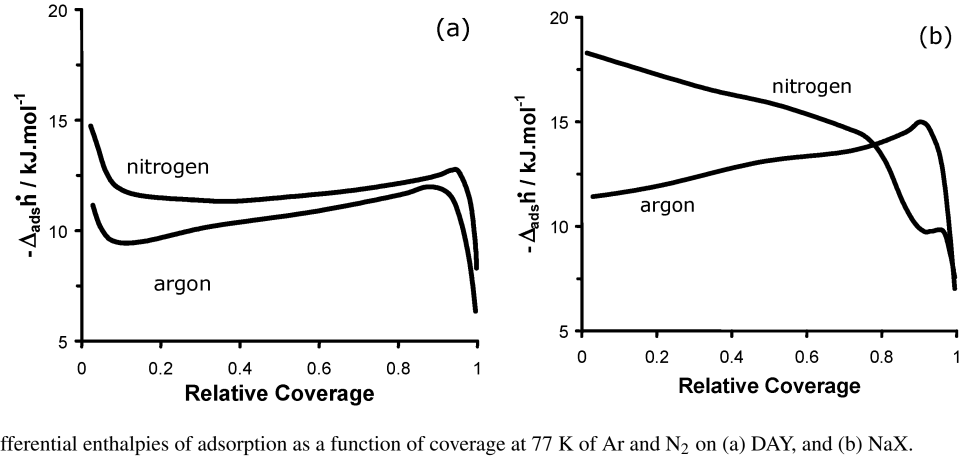

Figure 1. Differential enthalpies of adsorption as a function of coverage at 77 K of Ar and N_2 on (a) DAY, and (b) NaX.

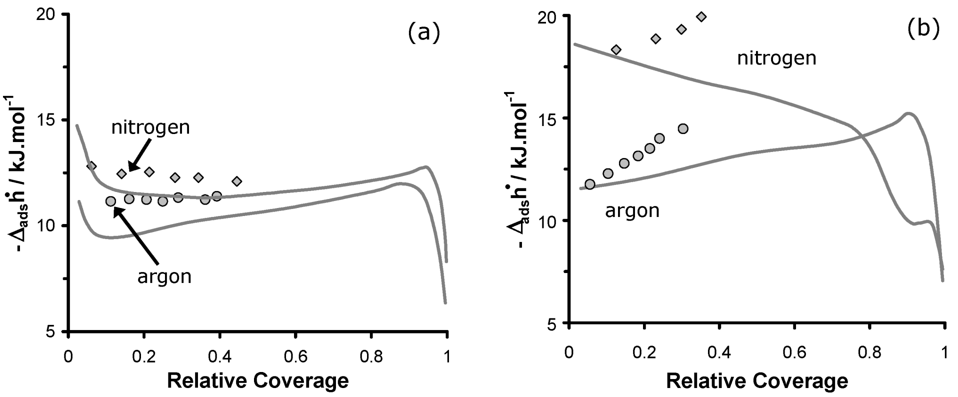

Figure 2. Differential enthalpies of adsorption (assuming excess quantities) at 302 K (symbols) and 77 K (continuous line) as a function of Ar and N_2 coverage (a) DAY, and (b) NaX.

micropores (calculated from the t-plot obtained with nitrogen at 77 K).

The experimental enthalpy curves are generally interpreted from three basic types of interactions. Interactions between the adsorbate and a typical energetically heterogeneous adsorbent will decrease with increasing coverage (Llewellyn, 2000). This is due to the preferential interaction of the adsorbate gas with strongest energy sites progressively occurring before interaction with weaker energy sites. Such interactions occur with the most solids encountered. The interaction of probe molecules with an energetically homogeneous surface, such as graphite, will occur with constant energy until full surface coverage. In each of these cases, one has to take into account the lateral interactions between adsorbed molecules that tend to increase as the quantity of adsorbed molecules increases.

The adsorption of argon and nitrogen on DAY (Fig. 1(a)) give rise to similar shaped curves that initially sharply decrease before a gradual increase until the end of micropore filling. This initial sharp decrease would seem to correspond to the adsorption at defect sites formed during the dealumination process. From the enthalpy curve it can be estimated that less than 10% of the adsorption occurs at these defects. Argon is considered not to interact with chemical heterogeneities as it has been shown for the adsorption on non-porous silicas (Aristov and Kiselev, 1963; Rouquerol et al., 1979; Ismail, 1992; Jelinik and Kovats, 1994) as well as on MCM-41 type samples (Llewellyn et al., 1997). Thus, the argon probes the textural defects formed during dealumination. The quadrupole moment of nitrogen further interacts with specific surface chemical sites such as residual silanol's.

Above a relative coverage of 0.1, the gradual increase in enthalpy curves for both argon and nitrogen corresponds to the combined "constant" interaction of the gas with a relatively homogeneous surface of the zeolite (other than the defects) and the increasing lateral interactions between adsorbate species. One would expect that both argon and nitrogen fill energetically equivalent sites distributed in the supercage. The sharp decrease in differential enthalpies occurs at the end of micropore filling where the values tend towards those of liquefaction.

The differential enthalpy curves of argon and nitrogen at 77 K on NaX differ from those on DAY. The curve obtained for argon (Fig. 1(b)) shows a constant increase that can be interpreted as the sum of interactions between adsorbate-homogeneous surface and adsorbate-adsorbate molecules. The values observed with argon are around 2 kJ $\cdot$ mol^{-1} higher with NaX with respect to DAY due to the higher field gradient caused by the presence of sodium and aluminium in the former structure. Nevertheless, no initial decrease in the differential enthalpies is observed in the case of NaX which suggests the absence of textural defects. The adsorption of nitrogen on NaX at 77 K (Fig. 1(b)) shows a constant decrease to a relative coverage of around 0.9 where a second short step is observed up to the end of the micropore filling process. This decrease in differential enthalpy would suggest that the nitrogen probes NaX as a heterogeneous surface. Considering this and the much higher values of differential enthalpies than those observed for argon, it is clear that the quadrupole moment of nitrogen probes the energetic heterogeneity due to the presence of sodium cations. The nitrogen initially adsorbs close to the sodium sites (Feuerstein et al., 1988) before occupying less energetic sites within the supercages. The step in the differential enthalpy curve has previously been observed (Rouquerol et al., 1971) and can be considered as the second step of the micropore filling process. The first step can be considered as the adsorption in the region around the cations and framework oxygen whereas the second step corresponds to the completion of the pore filling process in the space remaining at the center of the faujasite cages. Such an explanation is corroborated by NMR studies (Fonseca et al., 1999).

Adsorption at Ambient Temperature

The pseudo-differential enthalpies of adsorption as a function of relative coverage at 302 K are reported in Fig. 2 as symbols. These results are directly compared with the differential enthalpies of adsorption obtained at 77 K (continuous lines) from Fig. 1.

The measurements at 302 K of argon and nitrogen adsorption on DAY (Fig. 2(a)) each give rise, within experimental error, to constant differential enthalpy values. This suggests a compensation between decreasing adsorbate-*mildly heterogeneous* adsorbent interactions and increasing adsorbate-adsorbate interactions. The initial sharp decrease in enthalpy observed in the experiment at 77 K is not observed at 302 K due to the lack of points at low coverage. The adsorption of argon (Fig. 2(b)) on NaX gives rise to increasing enthalpies with coverage. Argon highlights interactions with a "homogeneous" surface along and increasing adsorbate-adsorbate interactions. The adsorption of nitrogen on NaX gives rise to almost constant values of adsorption enthalpy with coverage which would suggest that nitrogen interacts with a heterogeneous surface.

A comparison of the evolution of the enthalpy curves obtained at 302 K with those obtained at 77 K does not seem possible as the measured values differ. For a deeper understanding, closer investigation of the representation of adsorption phenomena is required. Note that in Figs. 1 and 2, the Gibbs Dividing Surface representation of adsorption has been used.

It is evident that when comparing the adsorption at 77 K with that at ambient temperature the phenomenological problem of type of representation of adsorption be addressed. Adsorption is defined in terms of "*the enrichment of material or increase in the density of a fluid in the vicinity of an interface*" (Gregg and Sing, 1982; Rouquerol et al., 1999). One can consider *excess* or *absolute* (Specovius and Findenegg, 1978; Fischer et al., 1978) quantities. Generally the concept of a Gibbs Dividing Surface or "GDS" is considered where an arbitrary dividing surface is chosen in the volume in which adsorption can take place. This implies that the quantity adsorbed is the amount of molecules retained by the surface at a concentration higher than that of the bulk gas. Such a representation of adsorption leads to *excess* quantities adsorbed. One would prefer to consider *absolute* quantities which would correspond to the total quantity of molecules close to the surface. These values however, are difficult to measure directly and one generally makes use of excess quantities. The relationship between these two quantities can be given by $n^a = n^\sigma + c.v^a$, where n^a is the absolute amount adsorbed, n^σ the excess amount adsorbed, c the concentration of adsorbate in the gas phase and v^a the volume of the adsorbed phase. In the case of zeolites it is possible to consider the total pore volume for v^a (Neimark and Ravikovitch, 1997; Pribylov et al., 1991). This total pore volume was obtained from the t-plots of the isotherms obtained at 77 K. The difference in "absolute" and "excess" amounts adsorbed is generally within magnitude of less than 1% for the adsorption at 77 K on microporous solids and in the present case, this difference is about 0.2%. For the adsorption at 302 K, differences in the range of 10 to 15% occur in the amounts adsorbed at 30 bars. These differences equally affect the differential enthalpies of adsorption.

The pseudo-differential enthalpies of adsorption as a function of relative coverage at 302 and 77 K assuming absolute amounts adsorbed are reported in Fig. 3. A comparison with Fig. 2 shows that the calculation using absolute quantities leads to a decrease in differential enthalpies of adsorption.

From the adsorption of argon and nitrogen on DAY (Fig. 3(a)) it can be seen that the values obtained at 302 K assuming absolute quantities coincide well with those obtained at 77 K. Considering the adsorption of argon on NaX (Fig. 3(b)), a relatively good agreement is again observed between differential enthalpy values obtained at 302 K assuming absolute quantities with those obtained at 77 K. The adsorption of nitrogen on NaX (Fig. 3(b)) is less straightforward. Whilst the differential enthalpy of adsorption extrapolated to zero coverage seems to show a fair agreement between each temperature, with increasing amounts adsorbed the enthalpies differ.

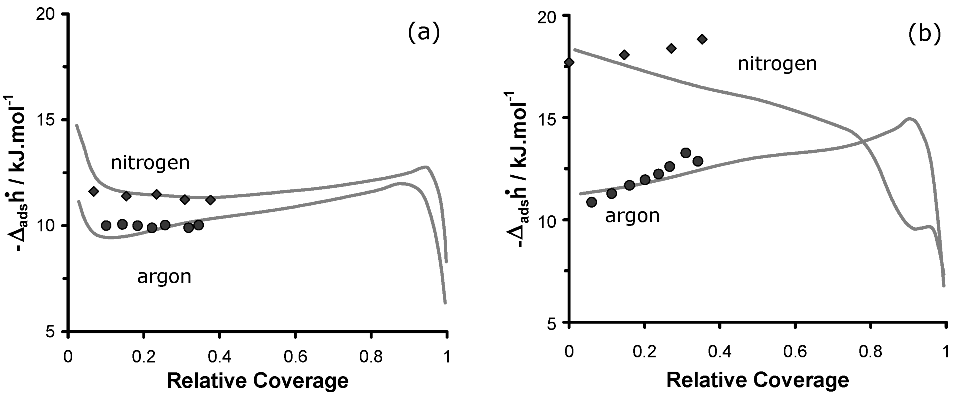

Figure 3. Differential enthalpies of adsorption, *assuming absolute quantities*, at 302 K (symbols) and 77 K (continuous line) as a function of Ar and N_2 coverage: (a) DAY, and (b) NaX.

Conclusions

The systems in this study were chosen to simplify the adsorption phenomena involved. As such it is possible to assume that the DAY behaves essentially as a non-specific surface and that argon acts as a non-specific probe molecule. The sodium cations in NaX act as specific adsorption sites and the quadrupole moment of nitrogen makes it a specific probe. Following Kiselev's (Kiselev, 1965) ideas one appreciate see that non-specific adsorption phenomena should occur for the Ar/DAY, N_2/DAY and Ar/NaX systems. Of the various systems in the present study N_2/NaX is the only one that should give rise to "specific adsorption" phenomena.

It is possible to speculate on the different behavior of nitrogen in the X-faujasite at each temperature. Whilst this probe should be more localized at 77 K, it may be more mobile at 302 K and statistically interact with more adsorption sites. Computer modeling will provide a deeper insight here.

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