Thermodynamics of hydrogen adsorption on calcium exchanged faujasite-type zeolites

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Abstract
A combination of variable-temperature infrared spectroscopy with volumetric gas adsorption measurements was used to study the thermodynamics of hydrogen adsorption, at a low temperature, on calcium-exchanged zeolites X and Y. Two adsorption regimes were considered: (i) localized adsorption of dihydrogen molecules on Ca\textsuperscript{2+} cation sites, and (ii) delocalized hydrogen adsorption following saturation of the Ca\textsuperscript{2+} adsorbing centres. For localized adsorption, the corresponding enthalpy change was found to be in the range of -12 to -15 kJ mol\textsuperscript{-1}, while the isosteric heat of delocalized adsorption was found to be in the range of -5 to -6 kJ mol\textsuperscript{-1}. These experimental results are discussed in the broader context of corresponding data for other alkaline zeolites, with a focus on correlation between adsorption enthalpy and entropy for the localized adsorption regime.

1. Introduction
The search for materials capable of safe and cost effective storage and on-board transport of hydrogen constitutes a major issue in the energy sector; among solutions being sought, porous adsorbents constitute a main line of current research [1,2]. These materials comprise mainly active carbons, including carbon nanostructures [3-8], and porous metal-organic frameworks (MOFs) and related materials [9-15]. Because of the high density of the aluminosilicate framework, which results in a low gravimetric uptake of the adsorbed gas, zeolites themselves are not likely candidates for on-board hydrogen storage and delivery. However, well known crystal structure and easy ion exchange make zeolites ideal materials for systematic studies on hydrogen bonding to a wide variety of metal-cation centres. And the realization that such studies can lead to useful insights for designing more prospective hydrogen adsorbents (e.g. MOFs having
exposed cation sites) lead to examine in detail hydrogen adsorption on zeolites, focusing attention on the gas-solid interaction energy; both experimental [16-21] and theoretical [22-26] studies were recently reported by several research groups.

We report here on experimental studies on hydrogen adsorption on calcium-exchanged faujasites, types X and Y. Gas adsorption isotherms (at 77.3 and 90.2 K) were used to derive the corresponding isosteric heat of adsorption and its variation with surface coverage, while variable temperature infrared spectroscopy was used to determine hydrogen adsorption enthalpy and entropy, thus achieving a fairly complete thermodynamic characterization of the gas adsorption process. The results are discussed in the broader context of available data for hydrogen adsorption on other alkali and alkaline-earth cation exchanged zeolites, with a view to gain further knowledge on the influence of exposed (coordinatively unsaturated) metal cations on hydrogen adsorption on porous solids, and also to highlight the important role played by the adsorption entropy.

2. Materials and methods

Faujasite-type zeolites X and Y were synthesized in their sodium forms by following standard procedures [27]; they had Si:Al ratios of 1.5 and 2.7, respectively. These parent materials were then repeatedly exchanged with a 0.5 M solution of calcium nitrate. Chemical analysis showed that practically total exchange of calcium for sodium was attained (only traces of sodium were found) in the case of the X zeolite, while for the Y zeolite only a partial exchange was attained. Hence, the calcium-exchanged samples are hereafter termed Ca-X and (Ca,Na)-Y, respectively. Powder X-ray diffraction of these samples showed good crystallinity in both cases, and all diffraction lines could be assigned to the corresponding faujasite-type structure [28].

Low temperature (77.3 and 90.2 K) hydrogen adsorption isotherms on Ca-X and (Ca,Na)-Y samples were measured on a Micromeritics ASAP 2010M gas adsorption analyser, up to atmospheric pressure. For these hydrogen adsorption measurements, the zeolite samples were previously outgassed under a dynamic vacuum (ca. $10^{-2}$ Torr, 1 Torr = 1.32 mbar) at 673 K overnight; subsequently, they were further outgassed for a short time at the same temperature under an ultra-high vacuum (ca. $10^{-6}$ Torr). Each adsorption isotherm was measured along 24 h, allowing for over one hundred equilibrium points to be registered. High purity hydrogen (premier quality) was supplied
by Metal Carbides. From the adsorption isotherms thus recorded, corresponding values of isosteric heat of adsorption were obtained by using the corresponding computer program supplied by Micromeritics.

For infrared (IR) spectroscopy, a thin self-supported wafer of each sample was prepared and activated (outgassed) in a dynamic vacuum (residual pressure < 10^{-4} Torr) for 3 h at 673 K inside a home made IR cell, described elsewhere [29], which allowed in situ sample activation, gas dosage and variable temperature IR spectroscopy to be carried out. After recording the blank spectrum of the zeolite wafer at liquid nitrogen temperature the cell was dosed with hydrogen, it was then closed, and spectra were taken at several fixed temperatures (within the range of 78 to 140 K) while simultaneously registering temperature and hydrogen equilibrium pressure inside the cell. For that purpose, the IR cell was equipped with a platinum resistance thermometer (Tinsley) and a capacity pressure gauge (Baratron). The precision of these measurements was about ±2 K and ±2×10^{-2} Torr, respectively. Fourier transform IR spectra were recorded, at 3 cm^{-1} resolution, by using a Bruker IFS66 instrument; 64 scans were accumulated for each spectrum.

It should be noted that localized adsorption of hydrogen molecules on zeolite alkali and alkaline-earth (extra-framework) cations leads to activation in the IR of the H–H stretching mode, which shows the characteristic IR absorption band red-shifted from the wavenumber value of the corresponding (Raman-active) mode of gas-phase molecular hydrogen [30-32]. This characteristic IR absorption band of adsorbed hydrogen, which usually appears in the range of 4050-4110 cm^{-1}, can be used to monitor adsorption thermodynamics by following the variable temperature IR (VTIR) spectroscopic method which in its very essence is outlined below in order to facilitate understanding of this article. Further details of the method can be found elsewhere [33,34].

At any given temperature, the integrated intensity of the characteristic IR absorption band (of adsorbed hydrogen) should be proportional to surface coverage, θ, thus giving information on the activity of both the adsorbed species and the empty adsorbing sites; simultaneously, the equilibrium pressure gives the activity of the gas-phase. Hence, the corresponding adsorption equilibrium constant, K, can be determined, and the variation of K with temperature leads to the corresponding values of standard adsorption enthalpy (ΔH^o) and entropy (ΔS^o). For deriving these values, integrated band
intensity, $A$, temperature, $T$, and equilibrium pressure, $p$, are considered to be interrelated by the Langmuir-type equation:

$$\theta = \frac{A}{A_M} = \frac{K(T)\ p}{[1 + K(T) \ p]}$$  \hspace{1cm} (1)

where $A_M$ stands for the integrated band intensity corresponding to full coverage ($\theta = 1$). Combination of Eq. (1) with the well known van’t Hoff equation (2) leads to Eq. (3) below:

$$K(T) = \exp(-\Delta H^0/RT)\exp(\Delta S^0/R)$$  \hspace{1cm} (2)

$$\ln\left[\frac{A}{(A_M-A)\ p}\right] = (-\Delta H^0/RT) + (\Delta S^0/R)$$  \hspace{1cm} (3)

By plotting the left-hand side of Eq. (3) against reciprocal temperature, for data obtained over a relatively large temperature range, corresponding values of $\Delta H^0$ and $\Delta S^0$, assumed to be temperature-independent, can directly be derived.

3. Results and discussion

Fig. 1 shows variable-temperature FTIR spectra, in the H–H stretching region, of hydrogen adsorbed on the zeolite Ca-X. A single H–H stretching band is seen, centred at 4082 cm$^{-1}$. This IR absorption band corresponds to the dihydrogen molecule polarized by Ca$^{2+}$ ions. Polarization, which is known to be the driving force for H$_2$ adsorption [21,23,24], renders IR-active the fundamental H–H stretching mode, which is only Raman-active (at 4163 cm$^{-1}$) for the free dihydrogen molecule. Such a polarization also brings about a bathochromic shift of $\nu$(H–H) which, in general terms, is proportional to the polarizing power of the cation involved [18,21,35]. However, the detailed structure of the cationic adsorbing centre (which includes the cation and nearby anions of the zeolite framework) is also known to have an influence on the magnitude of the bathochromic shift [21,30, 31]. Hence, the actual value of $\nu$(H–H) depends on both, the extra-framework cation involved and the zeolite being considered. Corresponding variable-temperature FTIR spectra of hydrogen adsorbed on the zeolite (Ca,Na)-Y are shown in Fig. 2. The IR absorption band of H$_2$ interacting with Ca$^{2+}$ ions is now seen at
An additional (much weaker) band was also seen at 4125 cm\(^{-1}\) (not shown) and assigned, in agreement with literature reports [31,36], to hydrogen interacting with Na\(^+\) ions. This latter band, which comes from an incomplete ion exchange of Ca\(^{2+}\) for Na\(^+\) in the parent Na-Y zeolite, is of no concern here.

From the sets of variable-temperature IR spectra shown in Figs. 1 and 2, the linear plots of Eq. (3) shown in Fig. 3(a,b) were obtained. From these linear plots, the standard adsorption enthalpy was found to be \(\Delta H^0 = -12.5\) kJ mol\(^{-1}\) for hydrogen on Ca-X, and \(\Delta H^0 = -15.0\) kJ mol\(^{-1}\) for hydrogen on (Ca,Na)-Y. The corresponding entropy change, \(\Delta S^0\), resulted to be -118 and -127 J mol\(^{-1}\) K\(^{-1}\), respectively. Estimated error limits are ±0.8 kJ mol\(^{-1}\) for \(\Delta H^0\) and ±10 J mol\(^{-1}\) K\(^{-1}\) for \(\Delta S^0\). It should be noted that for obtaining the plots shown in Fig. 3 \(A_M\) has to be known. An approximate value of this parameter was obtained, in each case, by recording IR spectra for increasing doses of hydrogen at 77 K and extrapolating the resulting Langmuir-type isotherm. This approximate value was then refined by plotting the left-hand side of Eq. (3) against reciprocal temperature for \(A_M\) values which were changed in small steps around the original value, and selecting (by linear regression) the best fit to the whole set of experimental data. The basis of this method was explained in detail elsewhere [34].

The volumetric hydrogen adsorption isotherms obtained at 77.3 K on both zeolites, Ca-X and (Ca,Na)-Y are shown in Fig. 4; while Fig. 5 depicts the corresponding adsorption isotherms at 90.2 K. In every case, these hydrogen adsorption isotherms show two distinct regions; a very steep (nearly vertical) region at a very low pressure, followed by a second region where adsorbed volume becomes more dependent on equilibrium pressure. This experimentally observed behaviour suggests that two different adsorption processes occur in each case; such distinct processes will be analysed in some detail below. Let us first point out that the very steep initial region of the adsorption isotherms precludes precise determination of the isosteric heat of adsorption, \(q_{iso}\), for the initial amounts of adsorbed hydrogen; in fact, unreasonable results were obtained when trying to calculate \(q_{iso}\) values corresponding to hydrogen adsorbed amounts smaller that about 10 cm\(^3\) g\(^{-1}\) (STP). Disregarding this region, Fig. 6 shows the evolution of adsorption heat (\(q_{iso}\)) against adsorbed volume for hydrogen on Ca-X and on (Ca,Na)-Y; as determined from the corresponding adsorption isotherms at 77.3 and 90.2 K.
For hydrogen adsorbed on Ca-X, Fig. 6 shows an initial plateau, up to \( ca. 37 \text{ cm}^3 \text{ g}^{-1} \) (STP), where \( q_{iso} \) has a constant value of 12 kJ mol\(^{-1}\); which coincides, within experimental error, with the value of \( \Delta H^0 = -12.5(\pm 0.8) \text{ kJ mol}^{-1} \) determined by the spectroscopic VTIR method (as stated above). In the case of (Ca,Na)-Y, no precise initial value of \( q_{iso} \) could be obtained, because the corresponding plateau was not reached within the usable data range. However, extrapolation of the curve shown in Fig. 6 suggests that for the smallest hydrogen doses \( q_{iso} \) should be significantly greater than 12 kJ mol\(^{-1}\), in agreement with the fact that a value of \( \Delta H^0 = -15.0(\pm 0.8) \text{ kJ mol}^{-1} \) was determined by VTIR spectroscopy. Note that infrared spectroscopy monitors only H\(_2\) molecules which are in direct (close) interaction with adsorbing cationic centres of the zeolite, and hence, the determined values of \( \Delta H^0 \) correspond to the adsorption regime up to saturation of all Ca\(^{2+}\) cations with adsorbed H\(_2\) molecules.

In both cases, H\(_2\)/Ca-X and H\(_2\)/(Ca,Na)-Y, the plot of \( q_{iso} \) against adsorbed hydrogen volume (Fig. 6) confirms that two different adsorption processes occur. First, adsorbed hydrogen molecules can come into direct contact with the zeolite Ca\(^{2+}\) cations, giving rise to localized adsorption involving the initial values of \( q_{iso} \) discussed above. For Ca-X, this process extends up to about 37 cm\(^3\) g\(^{-1}\) (STP) of adsorbed hydrogen, while for (Ca,Na)-Y it only reaches up to about 12 cm\(^3\) g\(^{-1}\). This is in consonance with the expected smaller amount of Ca\(^{2+}\) ions per gram of zeolite in (Ca,Na)-Y, as compared with Ca-X; because of a higher Si:Al ratio in (Ca,Na)-Y, and also because of incomplete exchange of calcium for sodium. Once the cationic hydrogen adsorbing centres are all saturated, \( q_{iso} \) drops to a value of 4 to 6 kJ mol\(^{-1}\); which is typical of unspecific (delocalized) adsorption processes involving only weak (London-type) interaction forces. Note that both, porous carbons and organic (porous) polymers, were repeatedly reported [1,37] to show a hydrogen adsorption heat in the range of 3.5 to 6.5 kJ mol\(^{-1}\). A further comment concerns the observed fact (Fig. 6) that, after the initial adsorption process, \( q_{iso} \) falls down somewhat less steeply for the H\(_2\)/(Ca,Na)-Y system than for H\(_2\)/Ca-X. This observed difference is likely to be due, at least in part, to the presence (in the first case) of some Na\(^+\) ions which, having a smaller polarizing power, are expected to contribute to hydrogen adsorption once all Ca\(^{2+}\) ions are saturated.

Additional information, particularly in regard to the weak interaction between hydrogen and the Ca-X zeolite, can be obtained from analysis of the hydrogen adsorption isotherms. Since the \( q_{iso} \) plot (Fig. 6) is composed of two regions, each of
them at a nearly constant $q_{iso}$ value, it should be possible to adjust the adsorption data by using a sum of two Langmuir type isotherms, that can be written as:

$$N = \left[ N_1 K_1/(1+pK_1) \right] + \left[ N_2 K_2/(1+pK_2) \right]$$  \hspace{1cm} (4)

where $N$ is the total amount of adsorbed hydrogen, $N_1$ and $N_2$ the adsorbed amount corresponding to each of the adsorption regimes and $K_1$ and $K_2$ the equilibrium constant of the corresponding Langmuir equation. Note that each of the two terms in the right-hand side of eqn. (4) has a rather different meaning. The first term corresponds to the relatively strong interaction that involves localized adsorption on cation sites; the second term is the analytical representation of non-localized adsorption in micropores, which also follows a Langmuir-type equation, as shown by Bathia and Myers for carbons [37]. Eq. (4) was used to fit the data of the adsorption isotherm (at 77.3 K) of hydrogen on Ca-X, depicted in Fig. 4. The result, shown in Fig. 7, confirms that a satisfactory fit could indeed be obtained. The fitting parameters corresponding to the strong interaction resulted to be $N_1 = 37.5(\pm0.5) \text{ cm}^3 \text{ g}^{-1} \text{ (STP)}$ and $K_1 = 79(\pm2) \text{ Torr}^{-1}$. The correctness of these values can readily be checked; the former coincides with the sudden change in $q_{iso}$ (Fig. 6), while the latter corresponds to a $\Delta G^0$ value of -2.80 kJ mol$^{-1}$ as obtained from the standard Gibbs equation, $\Delta G^0 = -RT \ln K_1$. Since the corresponding $\Delta H^0$ value is -12.5 kJ mol$^{-1}$, $\Delta S^0$ results to be -126 J mol$^{-1}$ K$^{-1}$, a value which coincides (within experimental error) with that of $\Delta S^0 = -118(\pm10)$ J mol$^{-1}$ K$^{-1}$ obtained independently by variable-temperature IR spectroscopy. For the second term of the sum in Eq. (4), which accounts for the weak interaction, the corresponding fitting parameters resulted to be, $N_2 = 159(\pm1.5) \text{ cm}^3 \text{ g}^{-1} \text{ (STP)}$ and $K_2 = 2.15(\pm0.05) \times 10^{-3} \text{ Torr}^{-1}$. This value of $K_2$ yields $\Delta G^0 = -3.93$ kJ mol$^{-1}$, and since $q_{iso}$ (which differs from $\Delta H^0$ by a mere RT term) has a value of about 5 kJ mol$^{-1}$ (Fig. 6), the corresponding entropy change results to be of about -122 J mol$^{-1}$ K$^{-1}$. A similar calculation would not go well for the H$_2$/(Ca,Na)-Y system, because (for the reasons already commented upon) the curve describing the experimentally determined variation of $q_{iso}$ as a function of hydrogen adsorbed amount cannot be neatly divided into two parts, each of them showing a (nearly) constant $q_{iso}$ value. Hence, modelling of the adsorption isotherm would imply putting at least three summing terms on the right-hand side of Eq. (4);
which would lead to having too many adjustable parameters, and to corresponding uncertainty arising from correlation effects.

Finally, it seems pertinent to analyse the results here reported for the standard adsorption enthalpy and entropy of molecular hydrogen on calcium-exchanged faujasites in the context of corresponding data for other alkaline zeolites. For that purpose, Table 1 summarizes recently reported data [38-40] of $\Delta H^0$ and $\Delta S^0$ for hydrogen adsorption on several alkali and alkaline-earth cation exchanged zeolites, together with those here reported for Ca-X and (Ca,Na)-Y. Note that these $\Delta H^0$ and $\Delta S^0$ values correspond to the process involving (cation) localized hydrogen adsorption, which is the only one measured by the VTIR method. These data clearly show, as discussed in detail elsewhere [39], that there is a non-linear correlation between hydrogen adsorption enthalpy and entropy, in the sense that (in general terms) larger values of $\Delta H^0$ involve larger values of $\Delta S^0$. Such a correlation can best be appreciated in Fig. 8, where $\Delta H^0$ is plotted against $\Delta S^0$. Clearly, the points corresponding to (Ca,Na)-Y and to Ca-X fit well into the correlation curve, thus giving further confidence on the results here reported.

Enthalpy-entropy correlation (also termed compensation) was also reported to occur in a wide range of chemical processes involving relatively weak interaction forces [41-43]. For the case of hydrogen adsorption on zeolites such a correlation reflects the fact that a stronger (enthalpy related) interaction between hydrogen molecules and zeolite adsorbing centres leads to a larger decrease of motion freedom of the adsorbed molecules, and hence to (entropy related) greater order of the system. It should also be noted that there is an intrinsic limit for $\Delta S^0$, since each adsorbed molecule can lose no more than all of its degrees of motion freedom, while in principle no definite limit exists for $\Delta H^0$; and this would explain the increasing slope of the curve representing the plot of $\Delta H^0$ against $\Delta S^0$ (Fig. 8) when $\Delta S^0$ increases more and more. $\Delta S^0$ data reported in Fig. 8 were obtained by VTIR spectroscopy, and they are referred to a standard state at 1 Torr (1.32 mbar) and 100 K, representative of the pressure and temperature range at which IR spectra were obtained. Since the entropy content of 1 mol of hydrogen at 1 Torr and 100 K is of about 175 kJ mol$^{-1}$, this would be the uppermost limit of $\Delta S^0$. However, this limit is not likely to be attained, because adsorbed hydrogen molecules are known to preserve a certain degree of rotational freedom, as well as vibration
against the zeolite adsorbing centre [18,31,44]. Whichever the case, however, we wish to remark that the observed correlation between enthalpy and entropy changes upon adsorption should be taken into account when designing potential adsorbents for storage and delivery of molecular hydrogen.

Conclusions

Thermodynamics of hydrogen adsorption on the zeolites Ca-X and (Ca,Na)-Y was studied by combining variable-temperature IR (VTIR) spectroscopy with volumetric measurements of hydrogen adsorption at 77.3 and 90.2 K. The case of Ca-X, the simplest of the two here examined, clearly shows that two types of interaction mode are possible for hydrogen molecules on cationic zeolites. The first of these modes involves a relatively strong electrostatic interaction of the adsorbed H\textsubscript{2} molecules with the exposed metal cation centres; such an interaction results in polarization of the adsorbed molecule, which renders the H–H stretching mode IR active. Moreover, for Ca-X, the interaction sites appear to be all of them equivalent and non mutually interacting, thus giving rise to a plateau in the initial portion of the plot of isosteric heat of adsorption against surface coverage. This indicates an ideal, Langmuir-type, nature of adsorption which is confirmed by the applicability of the VTIR spectroscopic method.

Further to that, a non specific (delocalized) adsorption mode takes place presumably once all of the exposed metal cations are saturated. This second adsorption mode, which corresponds to the filling of zeolite pores, shows a smaller interaction energy, similar to that reported for hydrogen adsorption on porous carbons and which can be assigned to weak (dispersion-type) interaction forces. It is remarkable that this second adsorption process can also be described by a Langmuir-type adsorption isotherm.

For the case of (Ca,Na)-Y, the results are somewhat blurred because of incomplete cation exchange. However, in general terms, the basic concepts stated above can still be applied. VTIR spectroscopy still shows an initially strong interaction due to localized adsorption of hydrogen molecules on Ca\textsuperscript{2+} cation centres, followed by a weaker interaction mode which should correspond to the ensuing pore filling at higher H\textsubscript{2} equilibrium pressure.

The standard adsorption enthalpy, $\Delta H^0$, for the strong interaction mode was found to be -12.5 and -15.0 kJ mol\textsuperscript{-1} for Ca-X and (Ca,Na)-Y, respectively. Such a relatively large values of $\Delta H^0$ were found to involve also correspondingly large values
of adsorption entropy: -118 and -127 J mol$^{-1}$ K$^{-1}$ for hydrogen adsorption on Ca-X and Ca-Y, respectively, referred to an standard state at 1 Torr and 100 K. Indeed, both systems, H$_2$/Ca-X and H$_2$/Ca(Na)-Y, conform to an overall enthalpy-entropy compensation effect already observed for hydrogen adsorption on other alkali and alkaline-earth cation exchanged zeolites.

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References


Table 1. Spectroscopic and thermodynamic data for hydrogen adsorbed on several zeolites. Error limits for $\Delta H^0$ and $\Delta S^0$ are $\pm 1$ kJ mol$^{-1}$ and $\pm 10$ J mol$^{-1}$ K$^{-1}$, respectively.

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<th>$-\Delta S^0$ (J mol$^{-1}$ K$^{-1}$)</th>
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Figure captions

**Figure 1.** Variable Temperature FT-IR spectra (zeolite blank subtracted) in the H–H stretching region, of H\(_2\) adsorbed on Ca-X. Temperature, in K, and equilibrium pressure (Torr, in brackets) are shown (1 Torr = 1.32 mbar).

**Figure 2.** Variable Temperature FT-IR spectra (zeolite blank subtracted) in the H–H stretching region, of H\(_2\) adsorbed on (Ca,Na)-Y. Temperature, in K, and equilibrium pressure (Torr, in brackets) are shown (1 Torr = 1.32 mbar).

**Figure 3a.** Plot of the left-hand side of Equation (3) against reciprocal temperature for H\(_2\)/Ca-X. R, linear regression coefficient; SD, standard deviation.

**Figure 3b.** As in 3a: H\(_2\)/Ca/(Ca,Na)-Y system.

**Figure 4.** Volumetric hydrogen adsorption isotherms at 77.3 K on Ca-X (squares) and on (Ca,Na)-Y (circles) zeolites. Black symbols denote adsorption and white ones desorption.

**Figure 5.** Volumetric hydrogen adsorption isotherms at 90.2 K on Ca-X (squares) and on (Ca,Na)-Y (circles) zeolites.

**Figure 6.** Evolution of adsorption heat (q\(_{iso}\), kJ mol\(^{-1}\)) against adsorbed volume (cm\(^3\) g\(^{-1}\), STP) for hydrogen on Ca-X (squares) and on (Ca,Na)-Y (circles); as determined for the corresponding adsorption isotherms at 77.3 and 90.2 K.

**Figure 7.** Volumetric hydrogen adsorption isotherm at 77.3 K on Ca-X zeolite (squares), with the corresponding fitting curve obtained according to Equation (4).

**Figure 8.** Standard adsorption enthalpy versus entropy for hydrogen adsorption on several cation exchanged zeolites. The two stars refer to values obtained in this work with Ca-X and (Ca,Na)-Y.
Figure 1
Figure 2
Figure 3a

Figure 3b
Figure 4
$T = 90.2 \text{ K}$

Figure 5

Adsorbed volume (cm$^3$ g$^{-1}$, STP) vs $p$ (Torr)

- $\text{H}_2$/Ca-X
- $\text{H}_2$/(Ca,Na)-Y
Figure 6
Figure 7

$T = 77.3$ K

**Adsorbed amount (cm$^3$ g$^{-1}$, STP)**

$p$ (Torr)

$H_2$/Ca-X
Figure 8