

Chromatographic Study of Adsorption of *n*-Alkanes on Zeolites at High Temperatures

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Henry constants, adsorption enthalpies, and entropies of C5–C10 *n*-alkanes were determined using the chromatographic method on BEA*, TON, MOR, and FAU type zeolites in the temperature range 200–375 °C. On all zeolites, the Henry constants of the linear alkanes increase exponentially with the alkane chain length. Adsorption enthalpies and entropies are related to the pore geometry and have an opposite effect on the Henry adsorption constant: smaller pore sizes lead to a strong increase of the adsorption enthalpy with the carbon number, which is favorable for the adsorption equilibrium. However, this increase of $-\Delta H_0$ with CN is accompanied by a high loss of degrees of freedom in small pores, leading to a strong increase of the adsorption entropy with chain length and counterbalancing the positive effect of the enthalpy on the Henry constants. On large-pore zeolites, the opposite effect is observed. The strongest increase of the Henry constants with the carbon number occurs on zeolites in which an intermediate increase of the adsorption enthalpy is accompanied by a moderate loss of degrees of freedom. For the zeolites studied, the rate at which the Henry constants increase with carbon number decreases in the order mordenite > beta > Y > CBV720 > ZSM-22 ~ CBV760.

Introduction

Zeolites find widespread application as catalysts and adsorbents in petrochemical processes. The understanding of the adsorption phenomena at temperatures relevant to zeolite catalysis is essential in the comprehension and the modeling of the reaction kinetics on zeolites. For obvious reasons, the adsorption of *n*-alkanes on zeolites has received a lot of interest.^{1–11} Techniques such as gravimetry,^{1,5,6,12,13} chromatography,^{9,14} combined gravimetry and calorimetry,^{7,8} and the isosteric technique^{2–4,15} were applied often. Most of these studies dealt with adsorption below 200 °C. The basic principles of hydrocarbon adsorption on zeolites are well understood and reported in many publications.^{16–18} Generally, a linear increase of the adsorption enthalpy with the carbon number of the *n*-alkanes at zero surface coverage was observed.^{3,6,7,9,12,19} In zeolite micropores, the adsorption enthalpy depends strongly on the pore shape and diameter. Stach et al.⁴ showed that the isosteric adsorption heat of *n*-decane increases exponentially with decreasing pore size for diameters below 100 Å. It was shown by McCullen et al.²⁰ that the adsorption heat of *n*-butane decreases linearly with increasing pore size on aluminophosphates.

The entropy of adsorption and the relation to the pore diameter and zeolite topology were also studied by several research groups. On faujasite zeolites, an increase of the adsorption entropy with the molecular weight of the *n*-alkanes was observed.^{1,4,13,21} A thermodynamic compensation effect

between the adsorption enthalpy and entropy of *n*-alkanes was observed in different studies, indicating that the stronger adsorption of longer *n*-alkanes is accompanied by a higher loss of degrees of freedom.^{8,21–24}

Experimental data on the thermodynamics of adsorption (especially on Henry constants) under catalytic temperatures are lacking in the literature. Moreover, most of the studies deal with adsorption of alkanes lighter than heptane. In our work, the adsorption thermodynamics of linear alkanes in the C5–C10 range have been determined in the temperature range from 200 to 375 °C on a range of zeolites with the chromatographic method.^{25–27} This technique allows us to measure adsorption properties at very low surface coverage and high temperatures in an easy and straightforward way, whereas with other techniques such as gravimetry, extrapolation to the zero-coverage limit is often required. Extensive cracking of probe molecules, which is often encountered with static techniques can be omitted by working at relative short contact times. The chromatographic technique was applied here to reexamine some basic principles already reported in the past and to investigate in detail the relationship among Henry constants, carbon number, zeolite topology, and Si/Al ratio at relative high temperatures.

Methodology

Two extreme models describing the adsorption of molecules can be considered: localized adsorption of the molecules on distinct adsorption sites (immobile adsorption) and nonlocalized adsorption (mobile adsorption).²⁸ For the localized adsorption model, the number of molecules in a unimolecular layer is determined by the number of adsorption sites. If one assumes that, at low surface coverage, these adsorption sites are provided

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TABLE 1: Henry Constants (mol kg⁻¹ Pa⁻¹) of *n*-Alkanes on Various Zeolites at 325 °C

carbon no.	mordenite	beta	HY	CBV720	CBV760	ZSM-22
5	1.35 × 10 ⁻⁵	1.65 × 10 ⁻⁵	4.90 × 10 ⁻⁶	3.17 × 10 ⁻⁶	1.42 × 10 ⁻⁶	8.29 × 10 ⁻⁷
6	4.32 × 10 ⁻⁵	4.62 × 10 ⁻⁵	1.10 × 10 ⁻⁵	5.80 × 10 ⁻⁶	2.74 × 10 ⁻⁶	1.28 × 10 ⁻⁶
7	1.45 × 10 ⁻⁴	1.29 × 10 ⁻⁴	2.29 × 10 ⁻⁵	1.05 × 10 ⁻⁵	4.64 × 10 ⁻⁶	2.17 × 10 ⁻⁶
8	4.80 × 10 ⁻⁴	3.69 × 10 ⁻⁴	4.73 × 10 ⁻⁵	1.90 × 10 ⁻⁵	7.99 × 10 ⁻⁶	4.00 × 10 ⁻⁶
9	1.61 × 10 ⁻³	1.08 × 10 ⁻³	9.92 × 10 ⁻⁵	3.91 × 10 ⁻⁵	1.37 × 10 ⁻⁵	7.60 × 10 ⁻⁶
10		2.97 × 10 ⁻³	2.08 × 10 ⁻⁴		2.53 × 10 ⁻⁵	1.38 × 10 ⁻⁵
11		1.03 × 10 ⁻²	4.28 × 10 ⁻⁴		4.54 × 10 ⁻⁵	2.51 × 10 ⁻⁵
12		2.91 × 10 ⁻²	9.08 × 10 ⁻⁴		8.54 × 10 ⁻⁵	

by the cations or the Brønsted acid sites, their concentration can be calculated in a straightforward way from the framework composition or from ammonia adsorption experiments. According to Atkinson and Curthoys,²¹ the relationship among localized adsorption entropy ΔS_0^θ , enthalpy ΔH_0 , temperature, and the Henry constant K' is given by

$$\ln(K') = \frac{-\Delta H}{RT_c} + \left[\frac{\Delta S_{0,local}^\theta}{R} + \ln\left(\frac{n_T}{2p^\theta}\right) \right] \quad (1)$$

The subscript 0 refers to the zero-coverage limit, n_T to the total number of adsorption sites, and p^θ to the standard state of the gas phase (chosen as 1 atm).

Experimental Section

Materials, Sorbates, and Columns. The experiments were performed with the H form of the zeolites except at higher temperatures where catalytic transformation of the probe molecules were significant. In those instances, the zeolites were used in the Na form. Zeolite beta, synthesized according to ref 29, was transformed into the Na form by ion exchange with aqueous solutes of ammonium chloride and subsequently with sodium chloride. ZSM-22 (Si/Al 30) was synthesized according to an established recipe,³⁰ calcined, exchanged with ammonium chloride, and deammoniated to obtain the H form. NH₄-mordenite (Zeocat, Si/Al ratio = 5) was transformed into the Na form by ion exchange with sodium chloride. NaY (Zeocat, Si/Al ratio = 2.7) was transformed into the H form by exchange with ammonium chloride and deammoniation. Dealuminated Y zeolites CBV720 (Si/Al ratio = 13) and CBV760 (Si/Al ratio = 30) were obtained from PQ zeolites. Brønsted acid site and cation concentrations were calculated assuming an ideal crystal structure.³¹

Activation of the adsorbents was performed by raising the temperature at a rate of 2 °C/min to 400 °C and maintaining this temperature overnight. All hydrocarbons used were of analytical grade and purchased from ACROS.

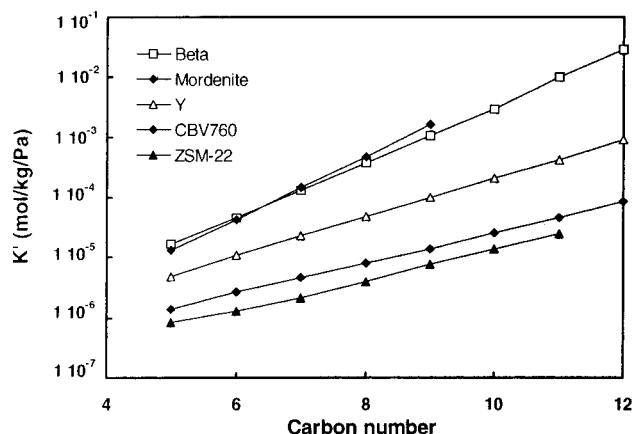
Results and Discussion

Henry Constants. In Figure 1, the Henry constants of the linear alkanes in the C5–C12 range at 325 °C are depicted as a function of the carbon number. The experimental values are given in Table 1.

The Henry constants of the linear chains increase exponentially with the carbon number and can be presented by a correlation of the following form:

$$K' = A e^{(B)(CN)} \quad (2)$$

with A and B as temperature-dependent constants and CN as the carbon number. The coefficient B in eq 2 depends strongly on the zeolite type. Table 2 gives the correlation between the carbon number and the Henry constants at 325 °C.

**Figure 1.** Henry constants of linear alkanes on zeolites Y, beta, ZSM-22, CBV760, and mordenite at 325 °C.**TABLE 2: Coefficients A and B of the Correlation $K' = A e^{(B)(CN)}$ between Henry Constants and Carbon Number for the Linear Alkanes at 325 °C^a**

	A (mol kg ⁻¹ Pa ⁻¹)		B	
	exptl	calcd	exptl	calcd
mordenite	3.34 × 10 ⁻⁸	5.31 × 10 ⁻⁸	1.20	1.13
Y	1.26 × 10 ⁻⁷	1.89 × 10 ⁻⁷	0.74	0.73
CBV720	1.39 × 10 ⁻⁷	2.24 × 10 ⁻⁷	0.62	0.59
CBV760	8.16 × 10 ⁻⁸	1.12 × 10 ⁻⁷	0.57	0.50
beta	7.44 × 10 ⁻⁸	8.98 × 10 ⁻⁸	1.07	1.04
ZSM-22	4.08 × 10 ⁻⁸	3.47 × 10 ⁻⁸	0.58	0.64

^a Experimental values and values calculated according to eq 5.

For zeolite Y, an increment of K' of about a factor 2 per extra carbon atom is noticed at 325 °C. For beta and mordenite, this increment is even more pronounced: a factor 2.9 for beta and even a factor 3.3 for mordenite are observed. On the Y zeolites, the Henry constants and the coefficient B decrease with increasing Si/Al (Figure 2).

Adsorption Enthalpy. The adsorption enthalpies, calculated from the temperature dependence of the Henry constants in the range 275–375 °C, increase almost linearly with the carbon number (Figure 3, Table 3, and Table 4), as was reported earlier for other zeolite systems:^{5–7,19,32}

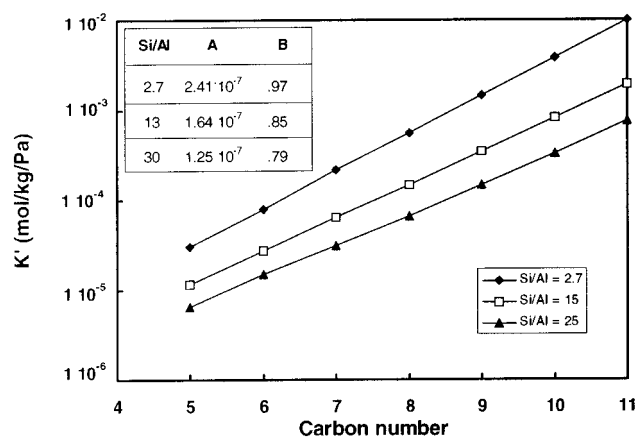
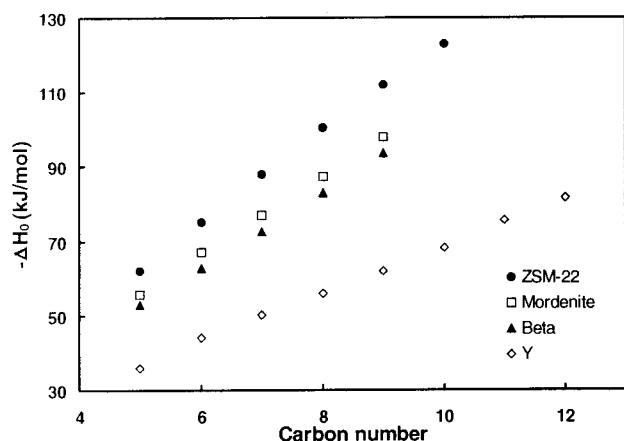
$$-\Delta H_0 = \alpha CN + \beta \quad (3)$$

The adsorption enthalpies reported here are generally lower than those reported in the literature (see Table 3). However, it should be mentioned that most of these measurements were performed at substantially lower temperatures.

The coefficients α and β of eq 3 are given in Table 4. The three faujasite zeolites HY, CBV720, and CBV760 have about the same adsorption enthalpy (see Table 3), although these three zeolites differ strongly in total Al content and nature of the Al.³³ Higher adsorption enthalpies are observed on beta and mordenite. These two 12MR zeolites lack the large supercages of 12

TABLE 3: Experimental Adsorption Enthalpies and Preexponential Factors of *n*-Alkanes for Adsorption on ZSM-22, Mordenite, Beta, Y, CBV720, and CBV760 and Values from Literature

	ZSM-22	H-TON ⁷	mordenite	H-MOR ²³	beta	Y	CBV720	CBV760	US-Ex ⁴
	$-\Delta H_0$ (kJ mol ⁻¹)								
<i>n</i> -pentane	62.1	71	55.7	59	53.0	36.1	35.1	36.7	45
<i>n</i> -hexane	75.0	81.5	67.1	69	62.7	44.2	41.9	43.3	53
<i>n</i> -heptane	87.9		77.0		72.6	50.1	49.1	50.3	
<i>n</i> -octane	101		87.3		82.9	55.9	55.5	56.5	67
<i>n</i> -nonane	112		98.1		93.7	62.0	60.5	63.2	
<i>n</i> -decane	123					68.3		69.2	
<i>n</i> -undecane						75.6		75.4	
<i>n</i> -dodecane						81.6		81.5	
	K_0 (mol kg ⁻¹ Pa ⁻¹)								
<i>n</i> -pentane	3.10×10^{-12}		1.83×10^{-10}		3.88×10^{-10}	4.22×10^{-9}	2.85×10^{-9}	9.69×10^{-10}	
<i>n</i> -hexane	4.59×10^{-13}		8.05×10^{-11}		1.54×10^{-10}	2.37×10^{-9}	1.37×10^{-9}	4.59×10^{-10}	
<i>n</i> -heptane	6.27×10^{-14}		2.30×10^{-11}		5.84×10^{-11}	1.56×10^{-9}	6.12×10^{-10}	1.86×10^{-10}	
<i>n</i> -octane	1.04×10^{-14}		9.00×10^{-11}		2.09×10^{-11}	7.95×10^{-10}	3.00×10^{-10}	9.35×10^{-11}	
<i>n</i> -nonane	2.31×10^{-15}		3.92×10^{-12}		7.87×10^{-12}	4.46×10^{-10}	1.93×10^{-10}	4.18×10^{-11}	

**Figure 2.** Henry constants of linear alkanes on faujasites Y (Si/Al ratio = 2.7), CBV720 (Si/Al ratio = 13), and CBV760 (Si/Al ratio = 30) at 233 °C.**Figure 3.** Adsorption enthalpy at zero coverage on beta, mordenite, Y, and ZSM-22.

Å diameter that constitute the framework of faujasites. In beta, the cavities have a diameter of 7.6 Å, and mordenite has unidimensional channels of 7 Å. The shorter distance between the adsorbed molecules and the zeolite framework in beta and mordenite results in a stronger dispersive interaction and thus a higher adsorption enthalpy.^{4,7,20} ZSM-22, which is the zeolite with the smallest pore diameter studied here (4.5 Å × 5.5 Å), has the highest adsorption enthalpy.

The increase in ΔH_0 per extra $-\text{CH}_2-$ group also depends on the zeolite type (see Table 4). Again, the zeolite with the smallest pore diameter shows the largest increase. On ZSM-22, the adsorption enthalpy increase with 12–13 kJ/mol per

TABLE 4: Coefficients α , β , γ , and δ of Correlation 5 among Henry Constants, Carbon Number, and Temperature for Linear Alkanes, and Values from Literature

	α (kJ mol ⁻¹)	β (kJ mol ⁻¹)	γ (J mol ⁻¹ K ⁻¹)	δ (J mol ⁻¹ K ⁻¹)
mordenite	10.5	3.5	8.21	48.9
Y	6.39	4.9	4.65	47.9
CBV720	6.44	3.3	5.86	35.3
CBV760	6.40	5.12	6.5	33.4
beta	10.0	2.58	8.13	36.2
ZSM-22	12.2	1.69	15.1	36.7
mordenite, ³² C3 → C6	9.3	12.9		
Y, ³² C3 → C6	7.3	9.4		
ZSM-22, ⁷ C3 → C6	10.8	16.55		
NaY, ²¹ C3 → C5	9.5	1.33		
US-Ex, ⁴ C2 → C6	7.3	7.6		

TABLE 5: Adsorption Entropies of *n*-Alkanes for Zeolites Y, CBV760, Beta, Mordenite, and ZSM-22

	$-\Delta S_{0,\text{local}}^{\theta}$ (J mol ⁻¹ K ⁻¹)					
	Y	CBV720	CBV760	beta	mordenite	ZSM-22
<i>n</i> -pentane	71.3	63.5	65.9	77.1	90.2	111
<i>n</i> -hexane	76.1	69.9	72.1	84.8	97.1	127
<i>n</i> -heptane	79.6	76.3	79.6	92.9	107	144
<i>n</i> -octane	85.2	82.2	85.3	101.4	115	159
<i>n</i> -nonane	90.0	86.5	92.0	109.6	122	171

extra carbon group. On beta, an increment of 10–11 kJ/mol was measured. On zeolite Y, the limiting adsorption enthalpy increases with 6–7 kJ/mol per additional carbon group, which is in good agreement with the values found in the literature (see Table 4).

Adsorption Entropy. A linear variation of the adsorption entropy (calculated according to eq 1) with the alkane chain length (Table 5 and Figure 4) is observed:

$$-\Delta S_{0,\text{local}}^{\theta} = (\gamma)(\text{CN}) + \delta \quad (4)$$

The coefficients of this equation are given in Table 4. The stronger interaction of the longer alkane chains with the zeolite structure results in an increasing loss of translational, rotational, and vibrational degrees of freedom.

For the three Y zeolites, the localized model results in similar values for the adsorption entropy, despite the large difference of about 1 order of magnitude in preexponential factors (Table 3). This indicates that, at low loadings, alkane molecules are adsorbed preferentially on the Brønsted acid sites or on the cations, as was previously reported by Eder and Lercher.⁷ Obviously, only one methyl group of the alkane molecule interacts with a Brønsted acid site or a cation, while the other

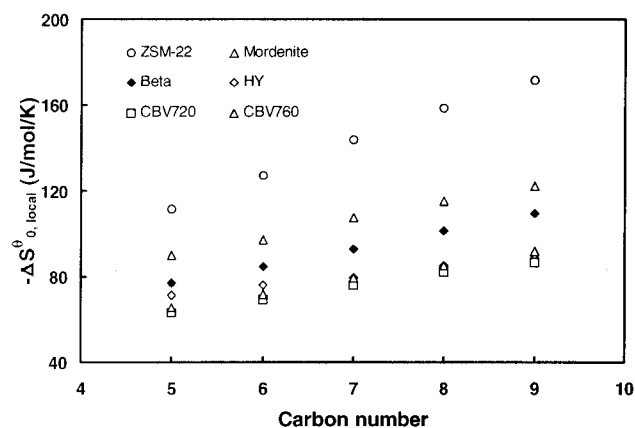


Figure 4. Localized adsorption entropies of *n*-alkanes against carbon number on Y, CBV720, CBV760, beta, mordenite, and ZSM-22.

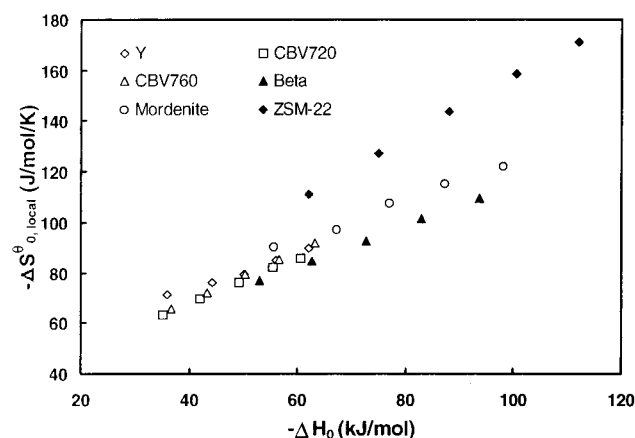


Figure 5. Relationship between localized adsorption entropies and enthalpies at zero coverage of *n*-alkanes on zeolites Y, CBV720, CBV760, beta, mordenite, and ZSM-22.

methyl groups interact with the lattice oxygen atoms. On zeolite Y, $-\Delta S_{0,\text{local}}^\theta$ increases with about $4.6 \text{ J mol}^{-1} \text{ K}^{-1}$ per added CH_2 group, while a somewhat larger increase is observed for CBV720 and CBV760 (5.9 and $6.5 \text{ J mol}^{-1} \text{ K}^{-1}$ respectively). It can therefore be assumed that alkane molecules occasionally jump from one acid site to another on zeolite Y. Owing to the lower acid site concentration on CBV720 and CBV760, this probability to jump to another site diminishes, leading to a faster increase of the adsorption entropy with the carbon number.

On beta and mordenite, the larger adsorption enthalpies are accompanied by a stronger increase of $-\Delta S_{0,\text{local}}^\theta$ with the carbon number, corresponding to $8\text{--}9 \text{ J mol}^{-1} \text{ K}^{-1}$. Finally, on the 10MR zeolite ZSM-22, the entropy of adsorption is significantly higher and increases with $15 \text{ J mol}^{-1} \text{ K}^{-1}$.

In Figure 5, a linear relationship between the adsorption entropy and enthalpy is observed. This effect is known as the isoequilibrium effect,²¹ which occurs when the Gibbs free energy ($\Delta G = \Delta H - T\Delta S$) is constant. Even more remarkable is that all 12MR zeolites reveal the same relationship between the adsorption enthalpy and the adsorption entropy. ZSM-22 (10MR), however, shows a steeper increase of $-\Delta S$ with $-\Delta H$.

Correlation for the Henry Constants. Equations 3 and 4 can be combined with eq 1 in order to obtain a general correlation for the Henry constants of the linear alkanes as a function of chain length and temperature:

$$\ln K' = \left(\frac{\alpha}{RT} - \frac{\gamma}{R} \right) \text{CN} + \left[\ln \left(\frac{n_T}{2p^\theta} \right) + \frac{\beta}{RT} - \frac{\delta}{R} \right] \quad (5)$$

With the parameters α , β , γ , and δ (Table 4), the coefficients A and B of the relationship $K' = A \exp[(\text{CN})(B)]$ (eq 2) can be calculated at any temperature. In Table 2, calculated values at 325°C are compared with the experimental values, resulting in a fairly good agreement. Although ZSM-22 has the highest adsorption enthalpy, B is rather low because of the large increase in adsorption entropy with CN. As a result of their intermediate adsorption enthalpies and adsorption entropies, zeolites beta and mordenite show the largest dependence of the Henry constants on the carbon number. Finally, on the Faujasite zeolites, the rather low dependence of adsorption entropy and enthalpy on CN results in an intermediate increase of K' with CN. Furthermore, on the faujasites, the exponential factor B decreases with increasing Si/Al ratio. This is caused by the diminished number of adsorption sites on the dealuminated zeolites. Since the correlation for the adsorption enthalpy yields the same parameters for the three investigated Y zeolites, eq 5 could be reduced to a two-parameter model with α and β as constants.

Conclusions

In this paper, it is shown that although the chromatographic method does not allow us to determine the loading dependence of the adsorption enthalpy and entropy in a simple manner as is possible with other static techniques, it provides a fast and straightforward way to determine adsorption properties at very low surface coverage and temperatures relevant to catalysis. By use of this technique, the influence of zeolite pore size and Si/Al ratio on the carbon-number dependence of Henry constants and adsorption enthalpies and entropies of *n*-alkanes in the C5–C10 range was determined on a range of representative zeolites. This study confirms the linear increase of $-\Delta H_0$ and $-\Delta S_0$ with CN as reported in other studies with techniques such as gravimetry, combined calorimetry and gravimetry, and the isosteric technique.^{4–7} Although the values for the adsorption enthalpies reported here are generally lower than those reported in the literature, the global trends that are generally accepted are found again in this study.^{4,7,21–23} Moreover, accurate values for the Henry constants at high temperatures could be obtained, which are scarce in the literature.

Our measurements indicate that the larger energetic interactions between the adsorbed molecules and the force field of the zeolite, which are observed on zeolites with smaller pores, are accompanied by a larger loss of degrees of freedom, reflected in higher adsorption entropies. On the basis of the observations, it was possible to derive a general relationship for the Henry constants, adsorption entropies and enthalpies, and the carbon number. It is our opinion that this rationalization of adsorption effects in zeolites can lead to a better understanding of catalytic effects on zeolites and eventually to a more rational design of catalysts.

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