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The Confinement Factor: A Thermodynamic Parameter to Characterize Microporous Adsorbents

JOERI F.M. DENAYER* AND GINO V. BARON
Department of Chemical Engineering, Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussel
joeri.denayer@vub.ac.be

Abstract. Low coverage adsorption properties of n-alkanes were used to characterize microporous adsorbents. A confinement factor Z, defined as the ratio of the increase of adsorption entropy with carbon number over the increase of adsorption entropy with carbon number, correlates well with the pore size.

Keywords: zeolites, adsorption, enthalpy, entropy, confinement, pore size

1. Introduction

Zeolites are by far the most selective catalysts and adsorbents used in refining and petrochemistry. Zeolites exist in many topologies, with one-, two- or three-dimensional pore systems, containing cages, lobes, side pockets, intersections of channels. The size of the pores varies between 3 and 20 Angström. A battery of techniques is available for studying the structure and chemical composition of zeolites (Jentys et al., 2001). Many spectroscopic methods are used, such as XRD to determine the zeolite crystal structure, adsorption isotherms are measured to determine the pore size, and parameters such as the constraint (Frilette et al., 1981) or the spaciousness (Ernst et al., 1988) index are obtained from catalytic reactions to classify zeolites according to their pore size.

Several authors have related the effective pore size of zeolites to the thermodynamics of adsorption of probe molecules. For apolar molecules, the adsorption enthalpy, reflecting the energetic interaction between the molecule and the zeolite force field, increases with decreasing pore size (Barrer and Sutherland, 1956; Thamm et al., 1983; Jänchen and Stach, 1985; Richards and Rees, 1987; Eder and Lercher, 1997, Hufton and Danner, 1993; Denayer et al., 1998; Smit and Siepmann, 1994). For such molecules, the interaction is mainly governed by Van der Waals interactions, which increase with decreasing distance between the interaction atoms or molecules. The adsorption entropy relates to the amount of freedom lost in the transition from the bulk phase to the adsorbed state. Generally, the smaller the pore in which the molecule is adsorbed, the higher the loss of translational and/or rotational freedom. For linear alkanes, a linear relationship between adsorption entropy and adsorption enthalpy exists, this effect being denoted as the "compensation effect" (Barrer and Rees, 1961; Katsanos et al., 1978; Atkinson and Curthoys, 1981; Eder and Lercher, 1997; Ruthven and Kaul, 1998; Denayer et al., 1998; Bond et al., 2000; Tümsek et al., 2003; Ford, 2005). With increasing carbon number N_c, *n*-alkanes are adsorbed more strongly as a result of the additive character of the Van der Waals interactions, generally leading to a linear increase of adsorption enthalpy with N_c. This linear increase of energetic interaction with N_c is accompanied with a linear increase of adsorption entropy: the more strongly a molecule is interacting, the more freedom it looses. Thus, when the adsorption entropy is plotted against adsorption enthalpy for a series of n-alkanes, a linear correlation is found. Interestingly, it has been found that the slope of this line is zeolite dependent (Eder and Lercher, 1997). The smaller the pore size, the more freedom is lost for a fixed adsorption enthalpy.

The adsorption enthalpy can be obtained in a direct way from calorimetric measurements, or indirectly

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*To whom correspondence should be addressed.

via the temperature dependency of the adsorption constant obtained with gravimetric, volumetric or chromatographic adsorption measurements. The adsorption entropy follows from the relationship between the adsorption equilibrium constant, the Gibbs adsorption enthalpy and the adsorption entropy and enthalpy (vide infra).

In this work, we have evaluated the use of the chromatographic technique for the characterization of the pore size of zeolites and other microporous materials. Low coverage adsorption properties (Henry adsorption constants, adsorption enthalpy and entropy) of C5–C10 *n*-alkanes were determined for a series of representative zeolites. A confinement factor, defined as the ratio of the increase of adsorption enthalpy with alkane carbon number over the increase of adsorption enthalpy with carbon number, is used to classify zeolites according to their pore size.

2. Methodology

The chromatographic technique was used to determine adsorption properties of n-alkanes. Columns of 0.25–0.40 m were packed with zeolite pellets. The materials were activated by heating to 400°C. For experiments at low coverage, in the linear part of the isotherm, the first moment of the chromatogram measured at the outlet of the column is related to the Henry adsorption constant K′ as (Ruthven, 1984):

$$\mu = \frac{L}{v_f}[(\varepsilon_{\text{ext}} + \varepsilon_{\text{macr}}) + (1 - \varepsilon_{\text{ext}} - \varepsilon_{\text{macr}})RT\rho_c K'] \tag{1}$$

with μ: the first moment, L: column length, v_f: superficial velocity in the adsorbent column, ε_{ext}: external porosity, $\varepsilon_{\text{macr}}$: macro porosity and ρ_c: the zeolite crystal density. All experiments were performed in the linear part of the isotherm, as shown by the invariance of the retention time with injection volume. The adsorption enthalpy at zero coverage (ΔH_0) was derived from the temperature dependency of the Henry constants (Suzuki, 1990):

$$K' = K'_0 e^{\frac{-\Delta H_0}{RT}} \tag{2}$$

Calculation of the adsorption entropy at zero coverage is less straightforward, and depends on some model assumptions. For example, if localized adsorption on distinct adsorption sites is considered, then the following equation can be developed (Atkinson and Curthoys, 1981; Denayer et al., 1998):

$$\Delta S^{\theta}_{0,\text{local}} = R\left[\ln K'_0 - \ln\left(\frac{n_T}{2p^{\theta}}\right)\right] \tag{3}$$

in which n_T refers to the total number of adsorption sites, and p^{θ} to the standard state of the gas phase (chosen as 1 atmosphere). This clearly shows that the experimentally determined pre-exponential factor of the van ‘t Hoff equation not only depends on the adsorption entropy, but also on n_T. For some materials, the number of adsorption sites is well defined, but mostly this is not the case, as even the nature or location of the sites is unknown, limiting the accuracy of Eq. (3) for the accurate and absolute determination of the adsorption entropy. A similar equation is obtained if non-localized adsorption on the two-dimensional zeolite surface is assumed, but instead of the number of sites, the surface area occurs in the equation expressing the relationship between the pre-exponential factor and the adsorption entropy (Atkinson and Curthoys, 1981). In general terms, the relationship between adsorption entropy and the pre-exponential factor of the van ‘t Hoff equation can be written as:

$$\Delta S_0 = R[\ln K'_0 - c] \tag{4}$$

in which c is a constant. Alternatively, the Gibbs free energy of adsorption at low coverage has been related to the Henry adsorption constants as (Schenk et al., 2003; Smit and Siepman, 1994):

$$\Delta G_0 = -RT\ln(K'\rho_c RT) \tag{5}$$

The adsorption entropy is calculated using the experimentally determined ΔH_0 and the Gibbs free energy (ΔG_0):

$$\Delta G_0 = \Delta H_0 - T\Delta S_0 \tag{6}$$

Although Eqs. (5) and (6) are very practical in their use, they do not take into account the effect of the adsorption site density. It was shown for several zeolites that alkanes are preferentially adsorbed on the Brønsted acid sites via dipole-induced hydrogen bonding (Eder et al., 1997). Although the crystal density is nearly independent of the Si/Al ratio, the number of Brønsted sites is proportional to the Al content of the zeolite, meaning that for identical structures with different Si/Al ratio, different Henry adsorption constants will be measured, an effect that is not captured by Eq. (5). In order to overcome the limitations of the above equations, the increase of the adsorption entropy with alkane carbon number (γ) rather than the absolute adsorption entropy is considered. Usually, it is found that the adsorption entropy decreases linearly with carbon number N_c:

$$-\Delta S_0 = \gamma\, N_C + \delta \tag{7}$$

Regardless of the adsorption model used, this gives in combination with Eq. (4):

$$-\Delta S_0 = -R[\ln K_0' - c] = \gamma\, N_C + \delta \tag{8}$$

allowing to calculate γ directly from the variation of the pre-exponential factor with N_c. The linear relationship between the carbon number of linear alkanes and the adsorption enthalpy can be represented as follows:

$$-\Delta H_0 = \alpha\, N_C + \beta \tag{9}$$

In the following, it will be investigated to what extent the linear relationships between adsorption entropy and enthalpy on one hand and the carbon number on the other hand (Eqs. (8) and (9)) are valid for several materials, and if the parameters α and γ describing these relationships are related to the zeolite pore size.

3. Results and Discussion

3.1. Effect of the Si/Al Ratio

Figures 1 and 2 show the variation of adsorption enthalpy at zero coverage and the logarithm of the pre-exponential factor of the van 't Hoff equation with N_c on ZSM-5 zeolites with different Si/Al ratio. Linear relationships are obtained for both properties. With increasing Al content, the adsorption enthalpy increases, and a difference of about 10 kJ/mol is measured for nonane between the samples with the lowest and highest Al content. This is related to the hydrogen bonding of the alkanes on the Brønsted acid sites, the number of which is proportional to the Al content (Arik et al., 2003). This hydrogen bonding induces a polarity in the alkane, leading to an additional interaction of 10 kJ/mol compared to non-localized adsorption (Eder et al., 1997). Since the adsorption enthalpy of n-alkanes is dependent on the zeolite composition, it cannot be used directly to classify zeolites according to their pore size. Table 1 gives the increase of adsorption enthalpy and adsorption entropy with N_c (α and γ) for the different ZSM-5 samples. Also these parameters depend on the composition.

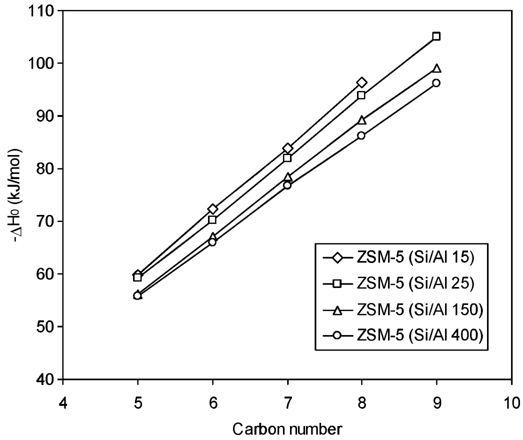

Figure 1. Zero coverage adsorption enthalpy as function of carbon number on ZSM-5 zeolites.

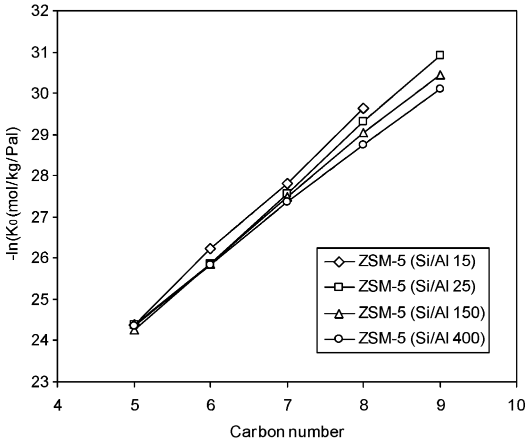

Figure 2. van 't Hoff pre-exponential factors as function of carbon number on ZSM-5 zeolites.

The *confinement factor* Z is defined as the ratio of α and γ, giving the loss of freedom for a fixed

Table 1. α, γ and confinement factor Z for ZSM-5 zeolites with different Si/Al ratio.

Si/Al ratio	α (kJ/mol)	γJ/(mol K)	Z $(1/K)$
15	12.10	14.38	1.19
25	11.54	13.76	1.19
150	10.76	12.95	1.20
400	10.14	11.99	1.18

interaction energy. In other words, Z quantifies the steric constraints imposed by a pore or cavity on the adsorbed molecules. Although α and γ vary significantly with the zeolite composition, their ratio Z is a constant (see Table 1), making this confinement factor an attractive parameter for pore size characterization:

$$Z = \frac{\gamma}{\alpha} \tag{10}$$

3.2. *Effect of Pore Size*

Adsorption enthalpies of n-alkanes at zero coverage are shown in Fig. 3 for a range of microporous materials with different pore topology. For all materials, the adsorption enthalpy increases linearly with carbon number.

The lowest adsorption enthalpies are obtained for zeolite HY, a faujasite have large supercages with a diameter of 12.3 Å, while the highest adsorption enthalpies were measured for ZSM-22, a 10 membered ring zeolite with pores of 4.4 × 5.5 Å. Zeolite ZSM-23 has slightly lower adsorption enthalpies than ZSM-22, in spite of its smaller pore size (4.5 × 5.2 Å). ZSM-57, another 10 MR zeolite with larger pores than ZSM-23 (5.4 × 5.1 Å), has comparable adsorption enthalpies. Mordenite, a 12 MR zeolite, has approximately the same adsorption enthalpy as the 10 MR ZSM-5 zeolite (Si/Al 150). Clearly, no classification is possible based on these data. When $-\ln(K_0)$ is plotted against the carbon number, linear correlations are found as a result of the linear increase of the adsorption entropy with carbon number, in accordance to Eq. (8) (see Fig. 4). Again, no direct correlation to the pore size is possible. For example, zeolite Beta, with its intermediate adsorption enthalpies between those of Mordenite and MCM-22 (Fig. 3) has relatively high pre-exponential factors (low $-\ln(K_0)$), only exceeded by those of HY.

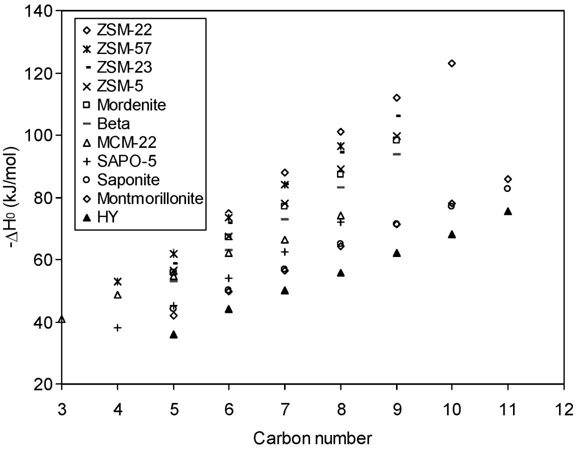

Figure 3. Adsorption enthalpy at zero coverage on a range of microporous materials.

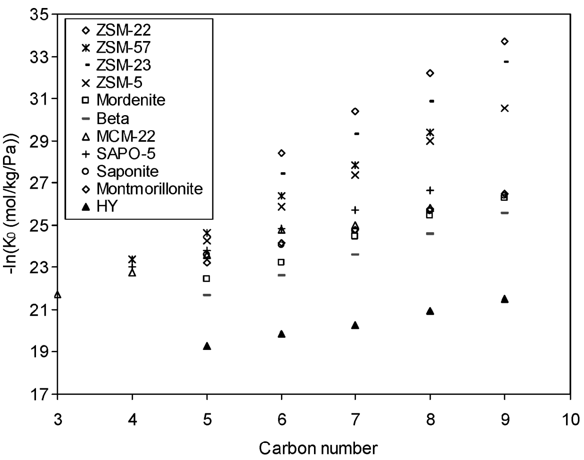

Figure 4. van 't Hoff pre-exponential factors as function of carbon number for several microporous materials.

Table 2 gives α, γ and Z determined from the experimental data using Eqs. (8–10), together with the size of the pores or cages of the material. These parameters are also shown in Fig. 5. Generally, Z increases with decreasing pore size. Z varies from 0.73 K^{-1} for HY to 1.26 K^{-1} for ZSM-23, the material with the smallest pore size. It appears that Z is very pore size sensitive, as it accounts for both energetic and entropic effects. For example, even between ZSM-22 and ZSM-23, a difference in Z is observed, although the pore diameters of both materials are very similar (4.4 × 5.5 Å and 4.5 × 5.2 Å respectively). This apparently negligible variation in pore size and shape has dramatic effects on the adsorption behavior at high pressure or in the liquid phase: whereas monobranched alkanes are able to fill about 60% of the internal pore volume of ZSM-22, they are completely excluded from the internal pores of ZSM-23 (Denayer et al., 2003).

Confinement factors were determined for microporous materials with more complex pore systems: MCM-22, consisting of large non-spherical cages (7.1 × 18.2 Å) and a narrow 10 membered ring (10 MR) system (4.0 × 5.9 Å) (Lawton et al., 1998). Although the energy factor α of this material is comparable to that of the relatively open 12 MR zeolites, the confinement factor is much higher as a result of the reduced mobility

Table 2. α, γ and confinement factor Z for microporous materials with different pore size.

	Pore size (Å)	α (kJ/mol)	γ (J/(mol K)	Z (1/K)
HY	Supercage: 12.3 × 12.3, Window: 7.3	6.4	4.7	0.73
Mordenite	7.0 × 6.5	10.5	8.2	0.78
Beta	5.7 × 7.5, 5.6 × 6.1, Intersections 7.6	10.0	8.1	0.81
SAPO-5	7.3 × 7.3	8.5	7.6	0.89
Saponite	Interlayer: 8.5 - Interpillar ?	7.3	6.6	0.90
Montmorillonite	Interlayer: 8.5 - Interpillar ?	7.4	7.4	6.9
MCM-22	18.2 × 7.1, 4.0 × 5.9	6.5	6.7	1.03
ZSM-57	5.4 × 5.1	10.9	12.7	1.16
ZSM-5	5.3 × 5.6, 5.1 × 5.5	11.5	13.8	1.20
ZSM-22	4.4 × 5.5	12.2	15.1	1.24
ZSM-23	4.5 × 5.2	11.8	14.8	1.26

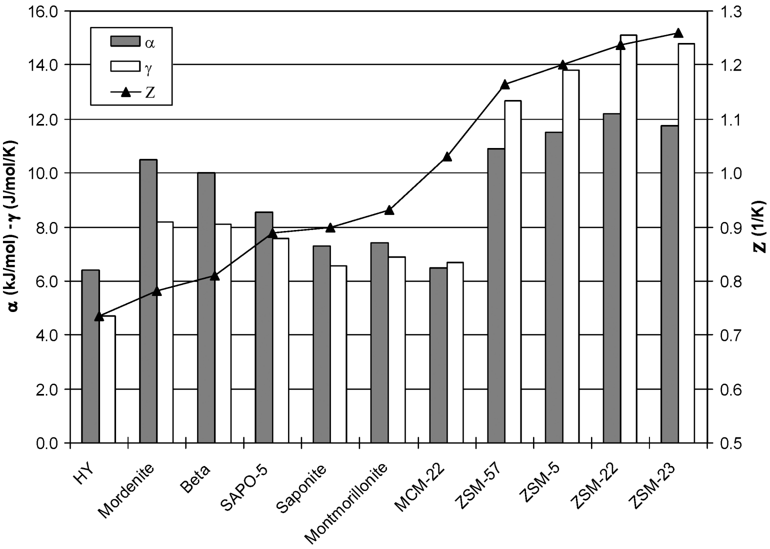

Figure 5. Adsorption enthalpy (α) and entropy (β) dependency on carbon number and confinement factor Z for n-alkane adsorption on microporous materials with different pore sizes.

of part of the molecules in interaction with smaller pore regions (Denayer et al., 2004). The pillared clays (Montmorillonite and Saponite) have confinement factors larger than the 12 MR zeolites, which is attributed to the relative small distance between the pillars bridging the clay layers. Although SAPO-5 has a larger pore opening than Mordenite and Beta, this material has a higher confinement factor. However, SAPO-5 has uniform cylindrical pores of 7.3 Å without side pockets or larger parts, whereas Mordenite has small side pockets in its channels, and Beta contains cavities formed by channel intersections with a diameter of 7.6 Å. The presence of these larger sections apparently decreases the confinement. A similar reasoning can be made for ZSM-5 and ZSM-57: the presence of intersections between linear and zigzag channels in ZSM-5 increases its effective pore diameter, leading to a smaller Z.

4. Conclusion

The confinement factor calculated from thermodynamic data obtained with the chromatographic technique correlates well to the pore size. The strength of this approach is that it tells how a material behaves under working conditions, yielding information complementary to that obtained by classical techniques.

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