

Adsorption of *n*-Alkanes on Silicalite Crystals. A Temperature-Programmed Desorption Study

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The adsorption mechanism of *n*-alkanes on silicalite has been studied by a modified temperature-programmed desorption (TPD) technique. These experiments are performed by thermogravimetry at constant hydrocarbon partial pressure and at slow heating rate. This work establishes the reversibility of the adsorption equilibrium, and it is demonstrated that TPD experiments occur under conditions that are very close to equilibrium. A quasi-chemical approach taking into account different adsorption sites provides a good modeling of the TPD curves. Sorption enthalpy and entropy variations of *n*-alkanes are obtained. The sorption data for *n*-butane to *n*-octane are in good agreement with adsorption literature data. Moreover, they provide relevant information on the adsorption mechanism and show that entropic effects are predominant.

Introduction

Silicalite is a microporous silica polymorph of ZSM5, which was discovered in 1977.^{1,2} The framework topology of ZSM5 is composed of a three-dimensional network of straight and sinusoidal channels as reported in 1978 by Kokotailo et al.^{3,4} The entrance to the channels is controlled by 10-membered rings of oxygen with dimensions reported as (0.54 nm × 0.56 nm) for the straight ones and (0.51 nm × 0.55 nm) for the zigzag ones.⁵

The potential application of silicalite as a shape-selective adsorbent for the separation of *n*-alkanes from isoalkanes is well established.⁶ In this respect, the adsorption of *n*-alkanes in silicalite has been studied in detail.^{7–14} Since the framework is mainly composed of silicon atoms and since the channels apertures are close to the *n*-alkanes kinetic diameters, the interactions are nonspecific and almost entirely the product of dispersion forces.¹⁵ As reported by Richard and Rees,¹⁶ these interactions must be dependent on the coverage, since several adsorption sites are involved in the adsorption process. This has been evidenced by Lohse et al.¹⁷ who studied *n*-hexane adsorption by calorimetry. More recently, Van Well et al.^{18,19} and Olson et al.²⁰ have performed temperature-programmed desorption (TPD) studies, which provided relevant qualitative insight in this area. However, the quantitative interpretation of these experiments has received much less attention. Rees et al.^{21,22} developed two different methods of analyzing TPD.

In this paper, we report results of a TPD study at quasi-equilibrium of *n*-alkanes in silicalite. These experiments were performed for *n*-butane to *n*-octane, and modeling of the results provided sorption enthalpy and entropy variations. These data are compared with adsorption data obtained by other more conventional methods.

TABLE 1: Properties of Samples

zeolites	1	2	3
crystals (μm ³)	2 × 1 × 0.5	20 × 5 × 4	100 × 50 × 50
Si/Al	380	> 1370	> 2360

Experimental Section

Materials. Three silicalite samples were used here. These samples exhibit various crystal sizes, shapes, and Si/Al ratios as depicted in Table 1.

Experimental Conditions. The TPD experiments were performed with a Setaram TAG 12 thermobalance. The temperature profile is reported in Figure 1. Each sample was previously heated at 673 K for 1 h in order to remove any adsorbate or template traces. The sample is then cooled to room temperature, and *n*-alkane molecules are introduced in order to saturate the sample with the adsorbate. The introduction of *n*-alkane is performed by circulation of helium (56 cm³/min) in a cell containing liquid *n*-alkane. The partial pressure of *n*-alkane is monitored with a thermostated bath. Normal butane, which is gaseous at normal temperature and pressure conditions, is directly introduced in the gas phase after being mixed with helium. Once the sample is saturated, the TPD is performed with a linear heating rate. Most of the experiments were performed at 5 K/min from 298 to 673 K, but other heating rates were also used. The *n*-alkane pressure is maintained during the experiment in order to ensure a constant alkane partial pressure within the sample. Since the desorbed amounts are very small because of the low adsorbent weight (20 mg), we may consider that the *n*-alkane partial pressure in the cell remains constant during the experiment.

Temperature-programmed adsorption (TPA) experiments were performed as well from 653 to 298 K with a cooling rate of 2 K/min.

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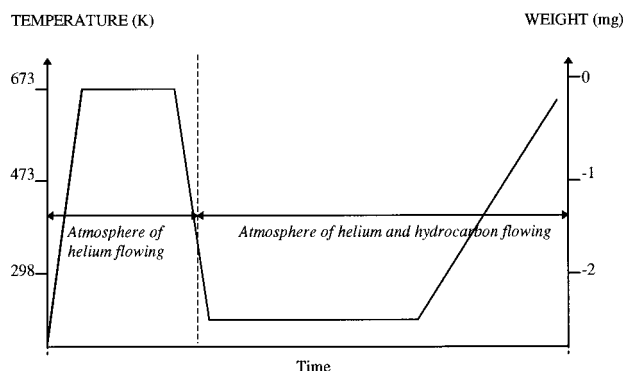


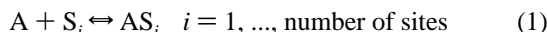
Figure 1. Experimental procedure.

Theory

Type I adsorption equilibrium is frequently described by the Langmuir isotherm. Cavalcante et al.⁶ obtained good modeling results for *n*-alkane adsorption in silicalite with this isotherm. However, they cannot predict adsorption for more than four molecules per unit cell, since the adsorption free energy must obviously depend on loading.

Figure 2 provides a simplified insight into the silicalite structure. The interconnection of the straight and zigzag channels gives rise to near-spherical cavities. Four occurrences per unit cell of each of these three sites must be considered. Depending upon the adsorbed molecules, channels as well as cavities are potential adsorption sites. For the general case of adsorption of a molecule, we must consider that the adsorption properties of these sites are a priori distinct and that a competition will occur as shown by several calorimetric studies.^{12,13,17,23}

A quasi-chemical approach provides a convenient description of this situation, and adsorption equilibrium on each site may be described by the following equations:



A is a sorbate molecule in the gas phase, S_i is a vacant site i , and AS_i is an adsorbed molecule on site i . One may consider S_i and AS_i as the quasi-chemical components of an ideal solution; that is, no interaction occurs between these components in the solution. This is reasonable, since the sites are clearly separated and since the molecules are not too long. Consequently, the activities may be assigned as concentrations so that the equilibrium constants are expressed as

$$K_i^{\text{ads}} = \frac{[AS_i]}{P[S_i]} \quad (2)$$

where P is the pressure of molecules A, $[AS_i]$ the activity of component AS_i in the solution, and $[S_i]$ the activity of component S_i in the solution. Moreover, only one molecule can adsorb in one site and there is no interaction between two adsorbed molecules. The balance equations relative to the number of adsorption sites may be added to this system:

$$N_i = [AS_i] + [S_i] \quad (3)$$

where N_i is the total number of site S_i in the adsorbent. This leads to the expression of the pure-component isotherm, where the adsorbed quantity q^{ads} is expressed in molecules per unit cell:

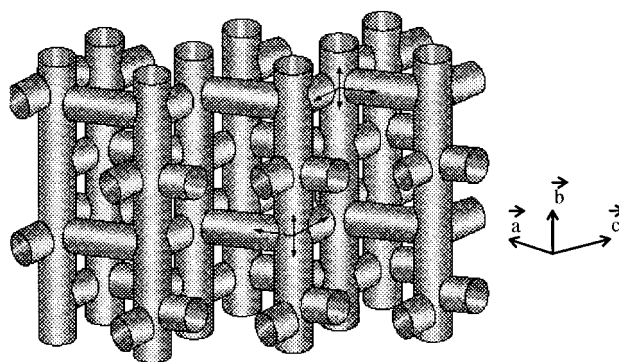


Figure 2. Schematic picture of the silicalite structure.

$$q^{\text{ads}} = 4 \sum_{i=1}^n \frac{K_i^{\text{ads}} P}{1 + K_i^{\text{ads}} P} \quad (4)$$

where K_i^{ads} is the adsorption equilibrium constant for equilibrium i . The heat of adsorption is calculated from $\Delta H_i^{\text{ads}} = \Delta U_i^{\text{ads}} - RT$ and according to the van't Hoff law:

$$K_i^{\text{ads}} = \exp\left(\frac{\Delta S_i^{\text{ads}}}{R} - 1\right) \exp\left(\frac{-\Delta H_i^{\text{ads}}}{RT}\right) \quad (5)$$

where ΔH_i^{ads} , ΔS_i^{ads} , and ΔU_i^{ads} are, respectively, the enthalpy, entropy, and internal energy variations associated with adsorption on site i .

Each site exhibits a single Langmuir adsorption behavior, and competition between these sites occurs. This expression contains $2n$ adjustable parameters, which are ΔH_i^{ads} and ΔS_i^{ads} . If we now consider the desorption process, the reverse equilibrium must be considered.

$$q^{\text{des}} = 4 \sum_{i=1}^n \frac{P}{K_i^{\text{des}} + P} \quad (6)$$

where K_i^{des} is the desorption equilibrium constant for equilibrium i . Considering that experiments are performed under quasi-equilibrium conditions and under constant pressure, we can use the derivative expression

$$\frac{dq^{\text{des}}}{dT} = 4 \sum_{i=1}^n \frac{\frac{\Delta H_i^{\text{des}}}{RT^2} \frac{1}{P} \exp\left(\frac{\Delta S_i^{\text{des}}}{R} - 1\right) \exp\left(-\frac{\Delta H_i^{\text{des}}}{RT}\right)}{\left(1 + \frac{1}{P} \exp\left(\frac{\Delta S_i^{\text{des}}}{R} - 1\right) \exp\left(-\frac{\Delta H_i^{\text{des}}}{RT}\right)\right)^2} \quad (7)$$

where ΔH_i^{des} and ΔS_i^{des} are the enthalpy and entropy variation associated with desorption from site i . At equilibrium and when we can consider that adsorption is reversible,

$$\Delta H_i^{\text{des}} = -\Delta H_i^{\text{ads}} = -\Delta H_i \quad \text{and} \quad \Delta S_i^{\text{des}} = -\Delta S_i^{\text{ads}} = -\Delta S_i \quad (8)$$

where ΔH_i and ΔS_i are the enthalpy and entropy variation of sorption. However, eq 8 cannot be generalized for all molecules. For example, complete isotherms for aromatics²⁴⁻²⁶ showed that adsorption and desorption equilibria are different.

Results

Validation of the Experimental Conditions. Several TPD experiments were performed for *n*-hexane on samples 1–3 for

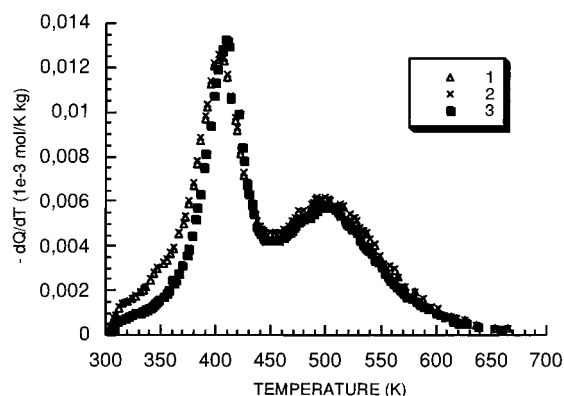


Figure 3. TPE curves obtained for various silicalite crystals for *n*-hexane.

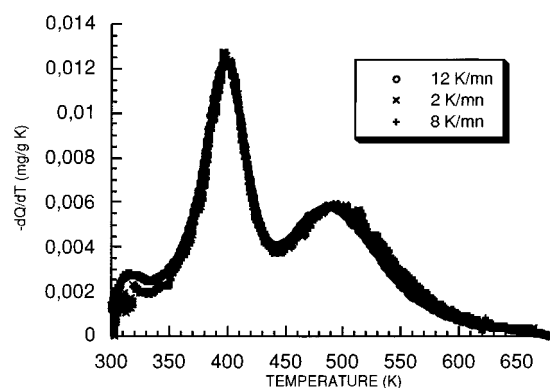


Figure 4. TPE curves obtained for various desorption rates for *n*-hexane.

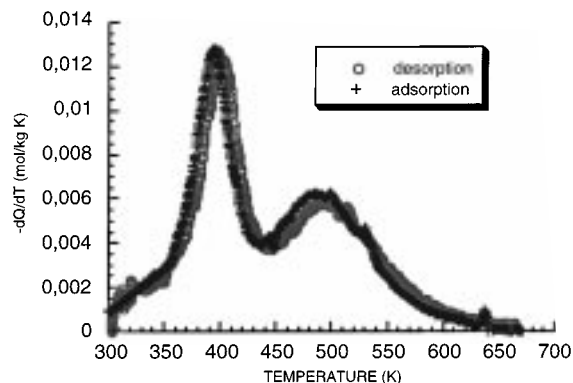


Figure 5. Comparison between adsorption and desorption measurements for *n*-hexane.

comparison. The corresponding results are plotted in Figure 3. They reveal that the desorption profiles are composed of several peaks. Whatever the sample, the desorption profiles are nearly the same. The sample size and the chemical composition do not affect the desorption spectra.

Heating rates were also varied. Three rates were used: 2, 8, and 12 K/min. The results obtained for *n*-hexane on sample 1 are reported in Figure 4. Identical desorption curves were obtained, indicating that the result is independent of heating rate in the range 2–12 K/min.

TPA experiment was also carried out with *n*-hexane and sample 1, with 2 K/min cooling rate. The comparison between this adsorption and desorption curves is plotted in Figure 5. Again, no major difference between the two curves can be noticed, indicating the reversibility of the phenomenon.

These results confirm that sample size as well as heating rate do not affect the TPD profiles. One may conclude from these

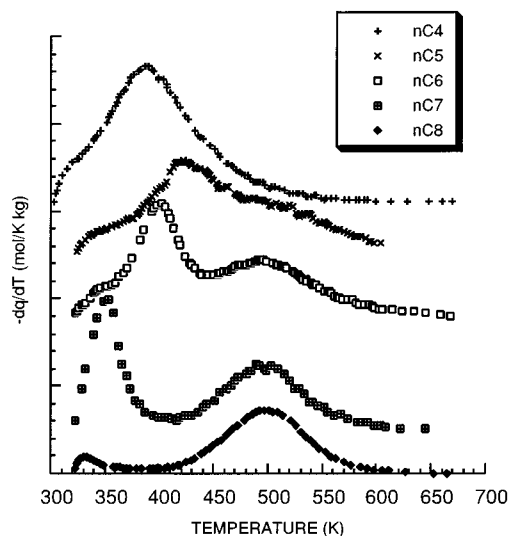


Figure 6. TPE curves obtained from *n*-butane to *n*-octane for sample 1.

TABLE 2: Sorption Capacities for ZSM5/Silicalite at 303 K

adsorbate	Q_{exptl} (molecules/unit cell)	$P_e/P_0 = P$
<i>n</i> -butane	8	0.10
<i>n</i> -pentane	8	0.38
<i>n</i> -hexane	8.10	0.10
<i>n</i> -heptane	7.90	2.7×10^{-2}
<i>n</i> -octane	5	7.5×10^{-3}

measurements that desorption occurs under conditions close to equilibrium and there is neither diffusional resistance nor readorption of desorbed molecules in the pore system. Moreover, the reversibility of equilibrium data is shown by the comparison between adsorption and desorption measurements. A heating rate of 5 K/min and sample 1 were chosen for subsequent experiments.

So, in this way, adsorption isotherms can be measured as a function of temperature. For clarity and a consistent nomenclature the present technique could be named temperature-programmed equilibration (TPE).

***n*-Butane-to-*n*-Octane Temperature-Programmed Desorption Results.** TPD curves from *n*-butane to *n*-octane were already reported by Rees et al.,^{21,22} Van Well et al.^{18,19} and Olson et al.,²⁰ but the quasi-equilibrium conditions were not established for these results. The similarity between our data and the data of the cited TPD studies shows experimentally that intrapore equilibrium exists during TPD of powders. We will now focus on the *n*-butane-to-*n*-octane results. First of all, we measured the adsorption capacities, which were obtained just before the desorption step. These data are reported in Table 2 and reveal that the saturation capacity is close to eight molecules per unit cell except for *n*-octane and *n*-butane under our experimental conditions. Subsequently, two-third of the silicalite sites are occupied for *n*-butane to *n*-heptane, while only about one-third is occupied for *n*-octane.

The desorption curves are plotted in Figure 6. The curves are separated from each other for the sake of clarity. Different behaviors are emphasized by these curves. A single-peak desorption profile characterizes *n*-butane and *n*-octane, while *n*-hexane and *n*-heptane clearly produce double-peak desorption profiles. In the case of *n*-pentane, a small inflection point in the curve at 450 K indicates the occurrence of two peaks (Figure 8). For all molecules, a small peak occurs at room temperature, which may be attributed either to surface or to nonconstant

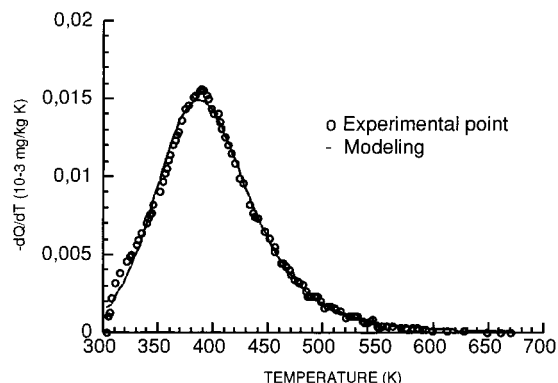


Figure 7. Comparison between experimental and calculated TPE curves from *n*-butane.

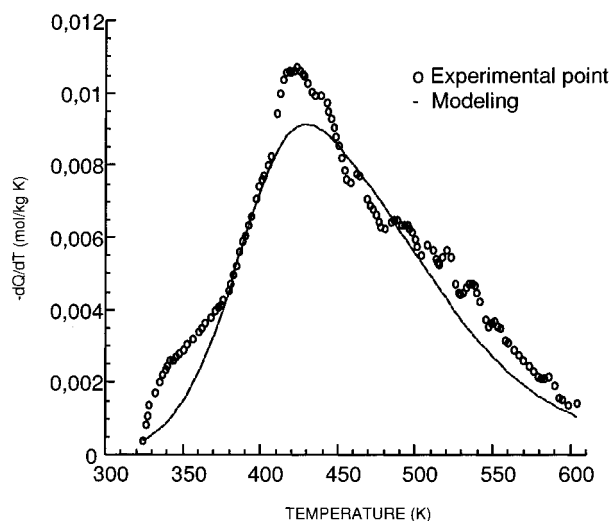


Figure 8. Comparison between experimental and calculated TPE curves from *n*-pentane.

heating rate at the beginning of the desorption. Thus, one does not take into account the low-temperature range.

These results suggest that a two-site model (with no interaction) could be sufficient to represent the desorption curves. If we take $n = 2$ in the expression for the rate of desorption, only four parameters must be adjusted in order to fit the various desorption curves. These parameters are the enthalpy and entropy variations for the two sites. For *n*-octane, since only four molecules per unit cell are adsorbed and since a single desorption peak occurs at high temperature, we considered $n = 1$. The results of the simulations of the TPE spectra are reported in Figures 7–11 and show very good agreement with results from the experiments. The corresponding enthalpy and entropy variations for sites 1 and 2 are reported in Table 3. Site 1 is the preferred site, that is, the site that is occupied first.

Gravimetric equilibrium isotherms²⁷ were measured for linear and branched C4–C7 alkanes on silicalite. Results are reported in Table 3 and are in good agreement with those obtained by the TPE technique.

Discussion

As we demonstrated earlier, the experiments are perfectly reversible and we can compare these sorption results with the data reported in the literature.

The literature data are reported for adsorption enthalpy variations in Table 4. It is worth noting that our data for *n*-pentane to *n*-octane are very close to those recently obtained by molecular simulations by Smit and Siepmann.²⁸ The

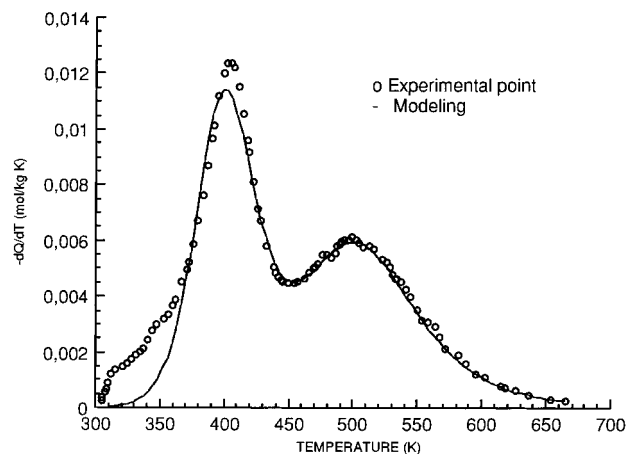


Figure 9. Comparison between experimental and calculated TPE curves from *n*-hexane.

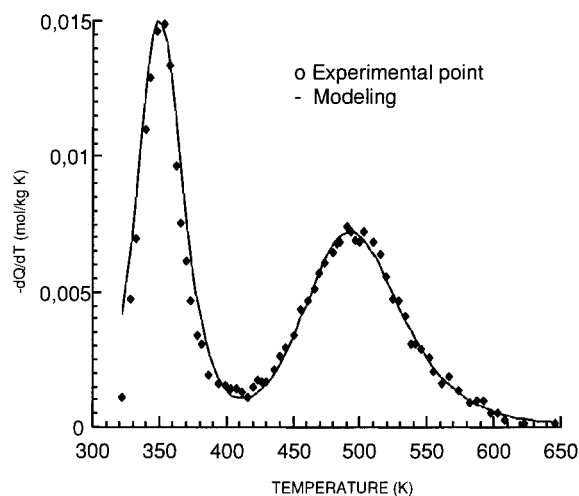


Figure 10. Comparison between experimental and calculated TPE curves from *n*-heptane.

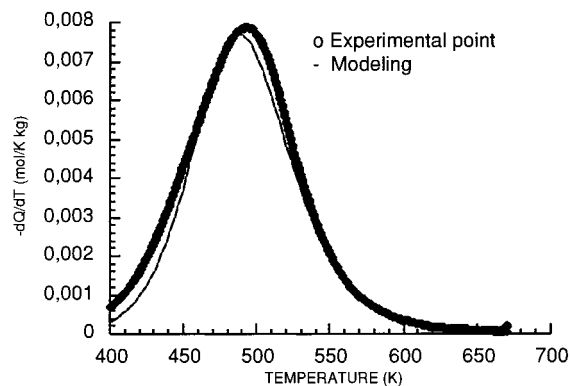


Figure 11. Comparison between experimental and calculated TPE curves from *n*-octane.

agreement with results of Lercher et al.,^{12,13} results of Sun et al.¹⁴ obtained by calorimetry and thermogravimetry, and results of Theodorou et al.²⁹ predicted by configurational-bias Monte Carlo integration is also good for *n*-hexane to *n*-octane except for *n*-butane and *n*-pentane. We obtain higher values compared with those of Lercher et al.^{12,13} and Theodorou et al.²⁹ and smaller for *n*-pentane compared with that of Sun et al.¹⁴ The calorimetric data²³ emphasize a small decrease in adsorption heat as a function of loading, which is also predicted by our model, since the heat of sorption for site 2 is always smaller than for site 1 (or higher in absolute value).

TABLE 3: Experimental Heat of Sorption and Variation of Entropy of Sorption of Various Alkanes in Silicalite/ZSM5^a

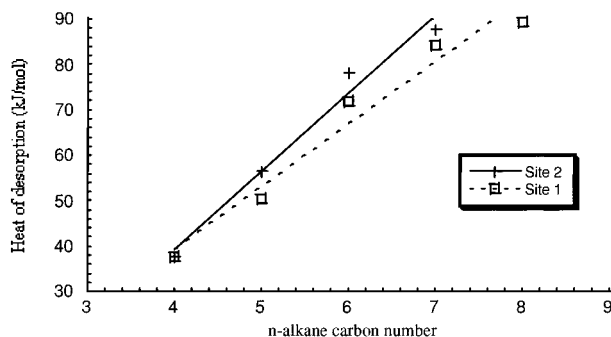
hydrocarbons	ΔH (kJ mol ⁻¹)		ΔS (J mol ⁻¹ K ⁻¹)	
	1st adsorbed site	2nd adsorbed site	1st adsorbed site	2nd adsorbed site
<i>n</i> -butane	-37.8	-37.8	-68.2	-68.2
<i>n</i> -pentane	-50.3	-56.4	-86	-116.3
<i>n</i> -hexane	-71.8 (-66)	-78.2 (-86)	-121.8 (-107.7)	-187.6 (-189)
<i>n</i> -heptane	-84.3 (-82.4)	-87.7 (-84.5)	-131.3 (-135.8)	-211.3 (-218.4)
<i>n</i> -octane	-89.4		-132.7	

^a Values in parentheses are determined by eq 6 from measured adsorption isotherms.²⁷

TABLE 4: Experimental Heats of Sorption and Variations of Entropy of Sorption of Various Alkanes in Silicalite/ZSM5 Given by Literature^a

hydrocarbons	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
<i>n</i> -butane	-54 ^b to -58 ^c [23], -48 [12]	-118 [12], 230 ^b to 150 ^c [23]
<i>n</i> -pentane	-58 [12], -70 [13], -41.8 [14]	-135 [13]
<i>n</i> -hexane	-69.8 ^b to -82 ^c [23], -62 ^b to -84 ^c [16], -84 [10], -72 [12], -82 [13], -70 [14], -70 [22]	-128 [12], -153 [13], -85 [29], 290 ^b to 180 ^c [23]
<i>n</i> -heptane	-101.2 [10], -84 [12], -94 [13], -83 [14], -82 [29]	-144 [12], -95 [29]
<i>n</i> -octane	-119 [10], -95 [12], -106 [12], -89 [14], -93 [29]	-157 [12], -105 [29]

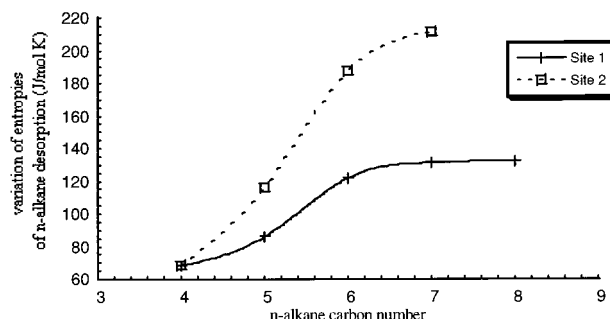
^a Reference numbers are in brackets. ^b Infinite diluted concentration in the zeolite. ^c Saturation of zeolite.

**Figure 12.** Enthalpies of *n*-alkane sorption on silicalite with different types of adsorption sites.

Some data concerning differential adsorption entropy variations were also reported by Stach et al.²³ (Table 4). Differential adsorption entropy values decrease with loading from 230 to 150 J mol⁻¹ K⁻¹ for *n*-butane and from 290 to 180 J mol⁻¹ K⁻¹ for *n*-hexane. Now it is clearly established that if adsorption heat is decreasing with increasing coverage, entropy variation must obviously decrease with coverage. The reason is that the free-energy variation for the low-coverage sites must be lower than for the high-coverage sites (or larger in absolute value). Therefore, concerning the variation of adsorption entropies, estimated Stach's values and our results are consistent with the adsorption-heat results. Our entropy variation values are also in good agreement with the values published by Lercher et al.^{12,13} (-153 J mol⁻¹ K⁻¹ for *n*-hexane and -144 J mol⁻¹ K⁻¹ for *n*-heptane), and they are smaller than those calculated by Theodorou et al.²⁹

We have reported our results as a function of the carbon number in Figure 12 for the enthalpy variation and in Figure 13 for the entropy variation. As it can be seen, the two sites exhibit enthalpy variations that are very close. In contrast, the entropy variations are very different for the two sites (except for *n*-butane). This indicates that entropy effects are strongly determinant for the location of the molecules on the sites. This is consistent with the earlier Van Well's^{18,19} qualitative interpretation of a constrained position of adsorbed molecules at high coverage.

Moreover, the enthalpy variation is linearly decreasing as a function of the carbon number. This is a very general trend for alkane adsorption in silicalite, since Titiloye et al.,¹⁰ Dubinin et al.,¹¹ Lercher et al.,^{12,13} Richards et al.,¹⁶ and Smit and

**Figure 13.** Variation of entropies of *n*-alkane sorption on silicalite with different types of adsorption sites.

Siepmann²⁸ showed that the heat of adsorption decreases linearly with CH₂ group number.

Location of Molecules inside the Structure of Silicalite.

The location of adsorbed molecules in the silicalite structure has received much attention in the past years. Despite the numerous papers concerning this subject, the localization of the molecules on the various adsorption sites as a function of loading is not well established.

From arguments based on adsorption isotherms, Jacobs et al.⁸ proposed that *n*-propane and *n*-pentane do not occupy a particular site and that *n*-hexane and *n*-octane first adsorb in the straight channels. In contrast, Richards and Rees¹⁶ assumed that the longer alkanes first adsorb in the zigzag channels. Moreover, Stach et al.²³ concluded from microcalorimetry experiments that no preferential adsorption takes place in silicalite for *n*-alkanes. In addition, energy minimization calculations performed by Titiloye et al.¹⁰ showed that *n*-alkanes are first adsorbed in the intersections and then in the straight channels. One may notice that entropy effects were ignored in all of these studies. This is a weakness, since we show that these effects are of influence. Lercher et al.¹² deduced from a gravimetric and calorimetric study that at low loadings molecules are located in the zigzag channels and can also populate the intersections for the longest ones. This can block the accessibility of straight channels. Molecules shorter than *n*-hexane can easily leave this accessibility. *n*-Hexane and *n*-heptane have to be confined in the zigzag channels, leading to an entropy loss so that straight channels can be filled. For molecules longer than *n*-heptane, the straight channels are not accessible. Molecular simulation was also extensively used for

n-alkanes. Entropy as well as enthalpy are taken into account with these techniques, but no consensus appears from the literature. For example, Nicholas et al.³⁰ showed a preferential adsorption in zigzag channels for *n*-propane, while for the short alkanes, June et al.,³¹ Smit and co-workers,^{28,32} and Theodorou et al.^{29,31} agree that the straight and the zigzag channels are equally likely and are preferred above the intersections. Finally, in studying diffusion through silicalite, Caro et al.³² suggested that short alkanes preferentially adsorb in the intersections while Jobic et al.³³ concluded that *n*-butane and *n*-hexane prefer the channels rather than the intersections.

Our results taking into account silicalite structure suggest that short alkanes up to *n*-butane have no preferential adsorption sites, since very small differences between the two sites are found. For longer *n*-alkanes (*n*-pentane, *n*-hexane, and *n*-heptane), we show clearly that $\Delta S_1 < \Delta S_2$ (in absolute value). This indicates that the molecules first adsorb on the less constrained sites. For *n*-octane, we find one type of adsorption site that is in a good agreement with literature data.^{18,21,28,34}

We are not able to determine the location of the sites, but one may conclude that, for these temperatures, the location of the molecules is determined by their entropy rather than by their enthalpy. However, a hypothesis could be proposed: considering that *n*-butane has the same length as the straight channels, one could suppose that these molecules fill identically the zigzag and the straight channels. For longer molecules, the lengths of the *n*-alkanes are greater than the lengths of the straight channels and adsorption free energy must depend on location.

Conclusion

That type of temperature-programmed desorption experiments was carried out for *n*-alkanes in silicalite. Experimental conditions such as desorption rates and crystal sizes were varied in order to establish that desorption occurs under conditions very close to equilibrium. In addition, temperature-programmed desorption as well as adsorption experiments showed that the system was reversible. We propose to name this technique temperature-programmed equilibration (TPE).

A quasi-chemical approach taking into account two adsorption sites with no interaction between adsorbed molecules provided a very simple modeling of TPD curves. The enthalpy and entropy variations associated with desorption from these two sites were compared with literature adsorption data. Our results are in close agreement with the recent molecular modeling work of Smit and co-workers^{19,28} and Theodorou et al.^{29,31} and also with the measurement and modeling of complete isotherms.²⁷

Silicalite can be considered as an energetically homogeneous adsorbent for *n*-butane. The heterogeneity occurs for five to eight carbons and increases with the carbon number.

The advantages of this method are the rapidity of data collection and the ease of analysis. The modeling and the discussion provide further insight into the adsorption mechanism of *n*-alkanes in silicalite.

Note Added in Proof. Very recently, Yang and Rees³⁵ reported isosteric heats of adsorption and differential molar

entropies of adsorption for *n*-hexane calculated from isosteres. Their results are in very good agreement with the results of our work.

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