

APPLICATION OF THERMAL ANALYSIS FOR EXPLAINING THE SORPTION OF BENZENE AND *n*-HEXANE ON SILICALITE

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Abstract

The origin of kinks (steps) on sorption isotherms was examined for the sorption of benzene and *n*-hexane on silicalite-1. In both cases sorption revealed the existence of two different binding sites. There was no equilibrium (or a very slow one), between molecules bound at different sites. Sorption energies within particular centres display more or less wide overlapping distributions leading to a single resultant isotherm. Depending on differences in binding energies and degree of overlapping, the resulting isotherms exhibit steps (benzene) or no steps (*n*-hexane).

In fact, the sorption isotherm of benzene being a sum of two elemental isotherms (Ω_1 and Ω_2) of different shapes is characterized by a 'kink', in contrast to *n*-hexane the elemental isotherms of which are of the same shape.

Keywords: benzene, isotherms, *n*-hexane, silicalite, sorption

Introduction

Silicalite-1 is a zeolite with the structure of ZSM 5. Its elementary cell consists of 94 tetrahedrons (SiO_4)⁴⁺ forming a three-dimensional structure and an internal channel system. There are two systems of circular channels, with a diameter of 0.54 ± 0.02 nm of zigzag arrangement and cross connected with elliptical channels, cross section $0.57-0.58 \times 0.51-0.52$ nm. Both types of channels are formed by ten-membered oxygen rings [1].

Because of the absence of cations and hydroxyl groups, silicalite-1 should be an energetically homogeneous micro-sorbent [2, 3]. Sorption of *n*-alkane mole-

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cules (kinetic diameter 0.43 nm) is supposed to occur due to their interaction with channel walls through dispersion forces [4]. The isotherms of *n*-alkanes published so far are simple, of the Langmuir type [5].

Contrary to the data on *n*-alkanes, the sorption of benzene and its derivatives is complex. At temperatures above 50°C they produce simple sorption isotherms of the Langmuir type, while at lower temperatures there is an inflexion in the adsorption curves (stepwise isotherms). The sorption of benzene on silicalite-I is similar to the type IV isotherm in the Brunauer classification [6, 7].

In addition to adsorption isotherms; adsorption isohores (isosteres) [8], X-ray and NMR spectra [9, 10] were obtained. To explain the sorption mechanism, two types of sorption sites for benzene on silicalite-I were proposed; one, at the intersection of sinusoidal and circular channels, and the other inside the circular channels. The stepwise isotherm is therefore explained by a two-site sorption mechanism of benzene, toluene and ethyl benzene opposite to the one-site sorption of *n*-alkanes producing a simple isotherm [8].

However, if a one-site sorption can be accepted for simple molecules of *n*-alkanes it is difficult to expect a two-site sorption (stepwise isotherm) for the even simpler nitrogen molecules [11].

Experimental

Silicalite-I was synthesized using Flanigen and Grose's method [12]. The synthesis was performed in an autoclave with teflon insert. The product was calcined at 650°C, in air, for 8 h and identified by X-ray diffraction, IR spectroscopy and nitrogen adsorption. A Philips diffractometer was used for X-ray studies and a Quantachrom Autosorb-6 for measuring nitrogen adsorption isotherms at 77 K.

The diffraction pattern of synthesized silicalite-I corresponds to highly crystallized monoclinic form (doublet between 24.6–25.0, 2 θ) without quartz, the presence of which has a remarkable influence on the total sorption capacity [13]. The adsorption isotherm of nitrogen at 77 K, is of stepwise type (published by others [11], not shown). This is important, as the presence of internal defects in the silicalite structure, such as hydroxyl groups leads to the absence of the inflection point in the adsorption isotherm of nitrogen [11]. The absence of hydroxyl groups was also confirmed by IR studies. The obtained total pore volume, 0.19 cm³, is in agreement with the total pore volume reported by Flanigen *et al.* [1].

Prior to sorption, silicalite-I was heated for 12 h at 400°C in vacuum (10⁻⁵ mmHg). The degree of sorption θ (percent) was determined by means of McBain Bakr's method. A Du Pont (DSC model 910 and TG model 951) thermal analyzer was used for desorption kinetic studies. The heating rate was 10°C min⁻¹ in a dry nitrogen flow, 15 ml min⁻¹.

The elementary curves of the complex desorption process were obtained by PDSC (Partial Differential Scanning Calorimetry) and PDTG (Partial Differen-

tial Thermogravimetry) methods as described by Vučelić *et al.* [14]. It was possible only through the combination of PDTG and PDSC to determine correctly the enthalpy of the elementary, basic desorption process.

Results and discussion

Figure 1 shows the DSC curve of benzene on silicalite-1. Two thermal processes occur (Fig. 1a) one in a relatively narrow range at a low temperature (below 50°C) and a broad one in the range of 50–110°C. Both are accompanied by the corresponding two thermodesorption processes (Fig. 2a). From these results it is obvious that benzene molecules are sorbed in silicalite at two different binding sites, forming two sorption complexes.

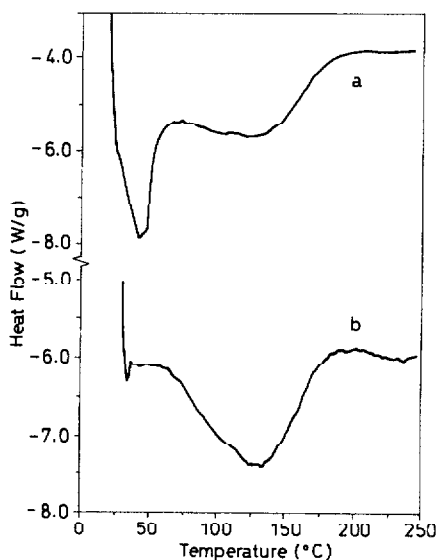


Fig. 1 Thermal curves of desorption of benzene from silicalite: a) DSC; b) PDSC of desorption of benzene from silicalite preheated at 45°C

It has been found by PDSC thermodesorption (Fig. 1b) that the position of the high-temperature peak is independent of the conditions of adsorption or desorption. The size and position of the low-temperature peak depend on the degree of coverage. There is no equilibrium between these two peaks. (After heating up to 45°C and then cooling, the low-temperature peak (Fig. 1b) will not appear even 2 h later in a repeated thermodesorption measurement.)

The DSC curve of *n*-hexane on silicalite-1, shown in Fig. 3a, reveals the existence of two independent sorption complexes, similarly to benzene. This is contrary to data [2, 3, 5, 15–17] about the uniform distribution of the silicalite-1 sur-

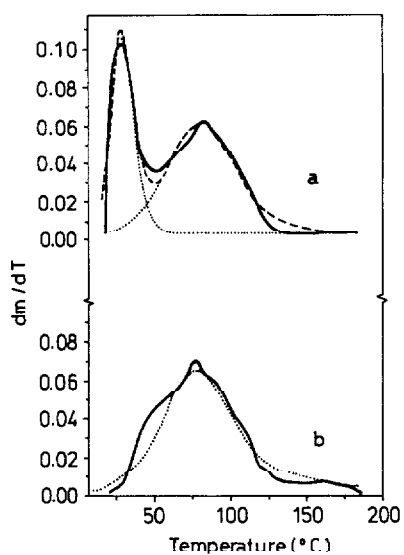


Fig. 2 PDTG desorption of benzene from silicalite; a) Full line: experimental thermodesorption, dashes: fitted by two Gaussian curves; $-(\Omega_1+\Omega_2)$; points: independent Ω_1 and Ω_2 from deconvolution; b) full line: sample preheated at 45°C, and points – fitted by Gaussian function

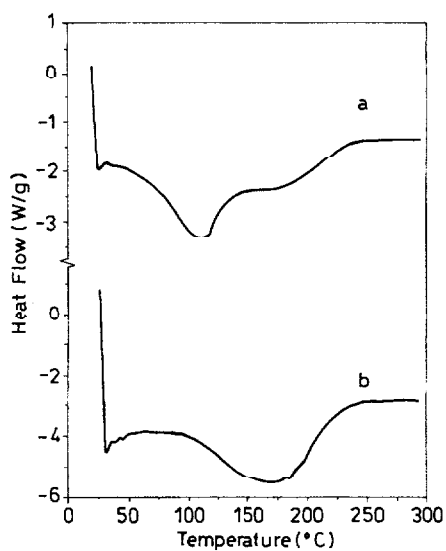


Fig. 3 Thermal curves of desorption of *n*-hexane from silicalite: a) DSC; b) PDSC of desorption of *n*-hexane from silicalite preheated at 90°C

Table 1 Enthalpies of desorption of benzene and *n*-alkane on silicalite-1

Sorbate	ΔH_1 (peak I)/kJ mol ⁻¹ Ω_1 -complexes	ΔH_2 (peak II)/kJ mol ⁻¹ Ω_2 -complexes	$\Delta H_{\text{evap.}}$ /kJ mol ⁻¹
Benzene	17.2	50.6	33.8
<i>n</i> -Hexane	65.0	95.9	28.9

face potential during the adsorption of *n*-hexane. From the partial DSC curve it is obvious, as it is with benzene, that the two sorption complexes are not in equilibrium (Fig. 3b).

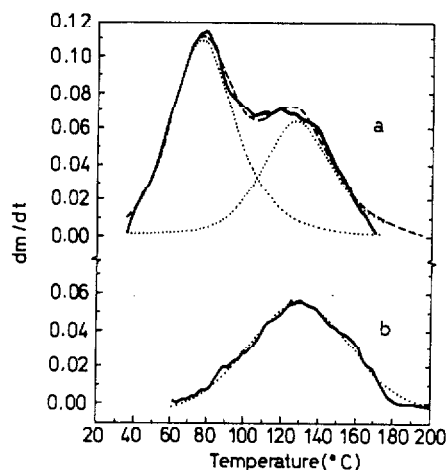


Fig. 4 PDTG of desorption of *n*-hexane from a silicalite surface. a) Full line: experimental thermodesorption; dashes: fitted by two Gaussian curves; $-(\Omega_1 + \Omega_2)$; points: independent Ω_1 and Ω_2 from deconvolution; b) full line: sample preheated at 90°C, and points: fitted by Gaussian function

The PDTG curves of desorption of benzene and *n*-hexane from silicalite 1 surfaces are shown in Figs 2b and 4b. In combination with the PDSC curves obtained simultaneously, Figs 1b and 3b, the molar sorption enthalpies of the high-temperature complexes, ΔH_2 , can be calculated directly. The results are presented in Table 1.

The high-temperature thermodesorption curves obtained for benzene and *n*-hexane are well fitted by a Gaussian function within experimental error (Figs 2b and 4b). This makes possible a straightforward deconvolution (within $\pm 2\%$), as shown in Figs 2a and 4a and calculation of the enthalpies of the low-temperature complexes. Simple subtraction of ΔH_2 from the total heat effect (experimental curves from Fig. 1a or 3a) and recalculating based on the corresponding mass loss (deconvoluted thermogravimetric curve from Fig. 2a or 4a) leads to molar sorption enthalpies of the low-temperature complex ΔH_1 (Table 1). (This

method, beside its simplicity allows to avoid the less precise method of ΔH_1 calculation from the low-temperature curve from DSC deconvolution.)

The obtained results can be summarized as follows:

1. There are two different thermodesorption processes for both benzene and *n*-hexane, in silicalite.

2. Preheating (45°C for benzene and 90°C for *n*-hexane, Figs 1b and 3b, respectively) removes the corresponding low-temperature thermodesorption processes, indicating a non-equilibrium relationship between them.

3. Sorbed molecules are bound in two different complexes, low-energy – Ω_1 (low-temperature desorption) and high-energy ones – Ω_2 (high-temperature desorption).

4. Wide energy distribution exists within these complexes. Broad – for Ω_2 (size 100–150 K) and a rather narrow one for Ω_1 (50–100 K), Figs 1 and 3, respectively).

5. In comparison to *n*-hexane, benzene is considerably more weakly bound, Table 1. The difference is especially significant for the Ω_1 type (enthalpy four times lower, the energy distribution within the complex four times narrower).

Using the experimental adsorption isotherm $a=f(p/p_0)$ (a is the adsorbed amount) and fractionated desorption curve as functions of the remaining amount of sorbent and temperature $\Delta m/m = f(T)$ it is possible to calculate the distribution of the adsorbed molecules between the two types of adsorption sites during the adsorption process.

The results are presented in Fig. 5. Curves Ω_1 and Ω_2 represent the adsorption isotherms of benzene and *n*-hexane on the two types of adsorption sites as a function of p/p_0 . Isotherms belonging to the sorption complex Ω_2 correspond to the Brunauer classification type I, for both benzene and *n*-hexane. However, the isotherm belonging to the sorption complex Ω_1 is of the type V for benzene, while for *n*-hexane it remains unchanged, type I. The existence of the kink (step) in a classical benzene isotherm and its absence for the sorption of *n*-hexane sorption (Fig. 5) results from this difference.

For both benzene and *n*-hexane, two different binding sites exist in non-equilibrium. This leads to simultaneous sorption on both types of binding sites, controlled only by the number of sites and equilibrium constant for molecules in gases and on sorbed Ω_1 and Ω_2 sites. The classical experimental isotherm, being the sum of simultaneous sorption on Ω_1 and Ω_2 will show a kink for benzene due to the different shapes of elementary sorption isotherms for Ω_1 and Ω_2 sorption processes. At low pressure the dominant sorption is Ω_2 (high binding enthalpy), while the significant sorption on Ω_1 (low binding enthalpy) starts “producing” steps in the sorption isotherm only after the first sorption is almost finished. Opposite to benzene, the sorption isotherms of *n*-hexane for Ω_1 and Ω_2 have the same shape (Brunauer type I) and a wide overlapping sorption energy distribution leads to a smooth sorption isotherm.

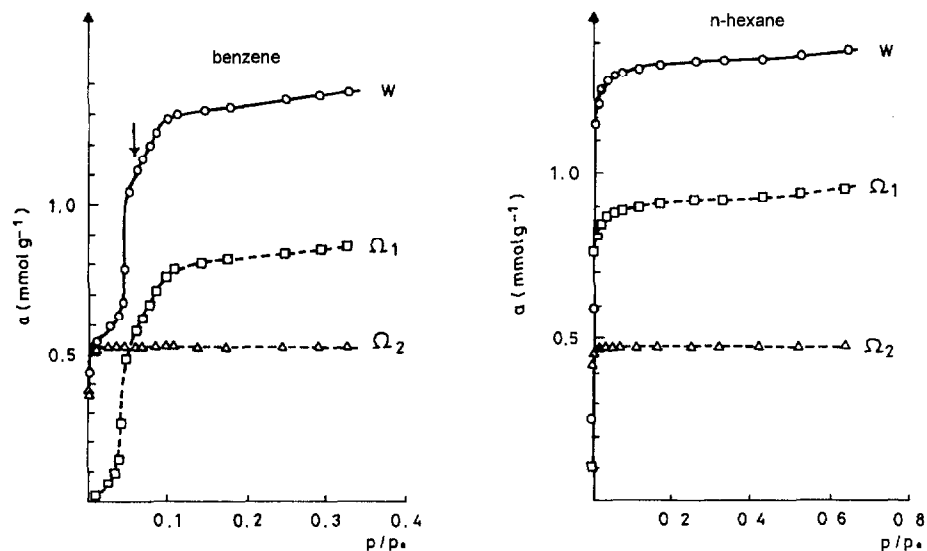


Fig. 5 Adsorption isotherms of benzene and *n*-hexane on silicalite, at room temperature: full lines – experimental gas sorption; open circles, $\Omega_1 + \Omega_2$. Reconstituted isotherm of elementally sorption process Ω_1 (quadrangles), and Ω_2 (triangles)

The presented results also make it easy to explain the absence of kinks in the sorption isotherms of benzene above 50°C.

Simply, there is no sorption on the site Ω_1 above 50°C (preheating at 45°C leads to elimination of the low-temperature peak in the DSC or DTG curve, Fig. 2). It is interesting to note additional small kinks (arrow in Fig. 5) in the sorption isotherms of benzene total and Ω_1 . Being reproducible, it is highly probable that it indicates three and not only two different binding sites for benzene. A shoulder in Fig. 2b for Ω_2 , also exists; however, due to high overlapping PDTG and PDSC resolution at present is not high enough to obtain the necessary parameters for good deconvolution.

Generally speaking, kinks or steps in sorption isotherms are to be expected whenever two or more binding sites exist on the surface in non-, or a very slow equilibrium. However, if the binding energies of the sites are close or overlapping due to wide distribution, kinks of steps will not be visible under standard experimental conditions.

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