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Citation for published version (APA):

van Well, W. J. M., Wolthuizen, J. P., Smit, B., Hooff, van, J. H. C., & Santen, van, R. A. (1995). Commensurate freezing of n-Alkanes in silicalite. *Angewandte Chemie - International Edition*, 34(22), 2543-2544.
<https://doi.org/10.1002/anie.199525431>

DOI:

[10.1002/anie.199525431](https://doi.org/10.1002/anie.199525431)

Document status and date:

Published: 01/01/1995

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Commensurate Freezing of *n*-Alkanes in Silicalite**

Willy J. M. van Well, Jillus P. Wolthuizen, Berend Smit, Jan H. C. van Hooff, and Rutger A. van Santen*

Computer simulations recently suggested the occurrence of a kind of phase transition in the adsorption of *n*-alkanes in zeolites.^[1] The described transition occurs as commensurate freezing of certain *n*-alkanes into the zigzag channels of silicalite. It was shown that *n*-alkanes that just fit in the zigzag channels, *n*-hexane and *n*-heptane, have to be first commensurately frozen in these channels before loadings higher than approximately half the maximum loading can be reached. Due to the additional loss of entropy, an increased pressure is needed to freeze the molecules into the channels. This increase in pressure is reflected as a step in the adsorption isotherms. The transition is also found in the adsorption isotherms of *n*-hexane and *n*-heptane in silicalite measured experimentally.^[2-4] In agreement with the additional loss of entropy, the occurrence of the step in the adsorption isotherms of *n*-hexane shows a temperature dependence.^[2, 3, 5] We have studied the behavior of *n*-alkanes as adsorbates in silicalite by temperature programmed desorption (TPD) and herein we discuss the results obtained; furthermore *n*-alkanes that have been predicted to show commensurate freezing behavior are compared with those that do not.

The synthesis of the silicalite sample was described in reference [6]. The elemental analysis revealed a Si/Al ratio greater than 4000 and a Si/Na ratio of 529. According to X-ray diffraction, the as-synthesized sample was highly crystalline. Calcination was performed in situ in a Setaram TG-DSC 111 apparatus (in which the adsorption and desorption measurements were also performed) in a mixture of helium and air (5% O₂) at 943 K for 1 h. The liquid sorbates, ranging from *n*-pentane to *n*-decane, were obtained from Janssen Chimica (Geel, Belgium). The purity of these sorbates was 99% or higher; *n*-butane 3.5 (purity 99.95%) was obtained from Hoek Loos (Schiedam, The Netherlands).

Adsorption into silicalite was achieved at room temperature by mixing the gaseous sorbate (*n*-butane) or a helium flow saturated with the vapor of the liquid sorbate in a pure helium flow of approximately 1.8 L h⁻¹. The rate of both the *n*-butane flow and the helium flow saturated with sorbate was about 0.6 L h⁻¹. Therefore, adsorption is achieved at a relative adsorbate pressure in the helium flow of at most 0.25. Saturation was reached within a few minutes for *n*-butane, while adsorption over 24 hours was needed to saturate the sample with *n*-decane. The obtained maximum loadings of the different sorbates and the micropore volumes calculated from these maximum loadings are given in Table 1. All loadings agree very well with the maximum loadings reported in literature, indicating that the crystallinity of the sample we studied was very good. However, the loadings reported by Flanigen,^[7] 1.9 mmol g⁻¹ for *n*-butane and 1.5 mmol g⁻¹ for *n*-hexane, were not reached.

Table 1. Maximum loadings of the *n*-alkanes on silicalite, and the micropore volume of silicalite calculated from these loadings. The micropore volume is calculated by using the density of the *n*-alkane at 20 °C relative to water at 4 °C. uc = unit cell.

<i>n</i> -Alkane	Maximum loading [molecule uc ⁻¹]	Maximum loading [mmol g ⁻¹]	Micropore volume [mL g ⁻¹]
<i>n</i> -butane	9.3	1.8	0.16
<i>n</i> -pentane	8.7	1.5	0.17
<i>n</i> -hexane	8.1	1.4	0.18
<i>n</i> -heptane	7.3	1.3	0.18
<i>n</i> -octane	5.4	0.93	0.15
<i>n</i> -nonane	5.1	0.89	0.16
<i>n</i> -decane	5.1	0.87	0.17

Temperature programmed desorptions were performed at a heating rate of 5 K min⁻¹ to a temperature of 723 K in a helium flow of 1.8 L h⁻¹. The temperature program was started immediately after the flow with sorbate was switched off. A blank run of the clean sample was subtracted from all TPD curves to correct for the temperature effect on the mass. All curves were measured on the same sample of activated silicalite with a mass of 10.39 mg.

A schematic drawing of silicalite (an all-silica zeolite) is given in Figure 1. As can be seen, it has a three-dimensional pore system consisting of intersecting straight and zigzag channels.

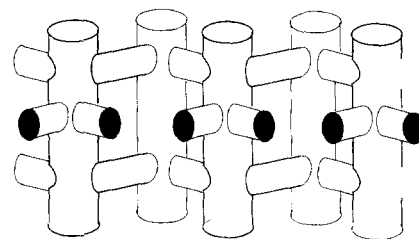


Fig. 1. Pore structure of silicalite.

In Figure 2, the TPD curves of the *n*-alkanes ranging from *n*-butane to *n*-decane are given. The differential mass loss (dm/dT) curves of *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane are

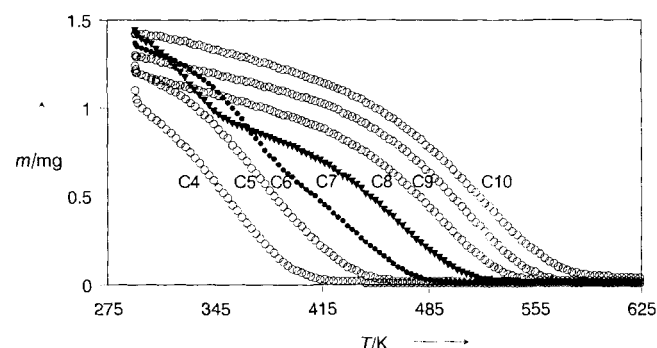


Fig. 2. Temperature programmed desorption curves of *n*-alkanes from silicalite; 10.39 mg silicalite; heating rate 5 K min⁻¹.

shown in Figure 3. For the sake of clarity in Figure 3, the differential mass curves are separated from each other. The curves of *n*-butane, *n*-nonane, and *n*-decane are similar to the curves of *n*-pentane and *n*-octane. Also for the sake of clarity, these curves are not displayed. The temperatures at which the maximum

[*] Prof. Dr. R. A. van Santen, Ir. W. J. M. van Well, Ing. J. P. Wolthuizen,

Prof. Dr. Ir. J. H. C. van Hooff

Schuit Institute of Catalysis

Laboratory of Inorganic Chemistry and Catalysis

Eindhoven University of Technology

P. O. Box 513, NL-5600 MB Eindhoven (The Netherlands)

Telefax: Int. code + (40)2455054

Dr. Ir. B. Smit

Shell Research B. V.

Koninklijke/Shell-Laboratorium, Amsterdam (The Netherlands)

[**] W. J. M. van Well is indebted to the Stichting Scheikundig Onderzoek in Nederland (SON).

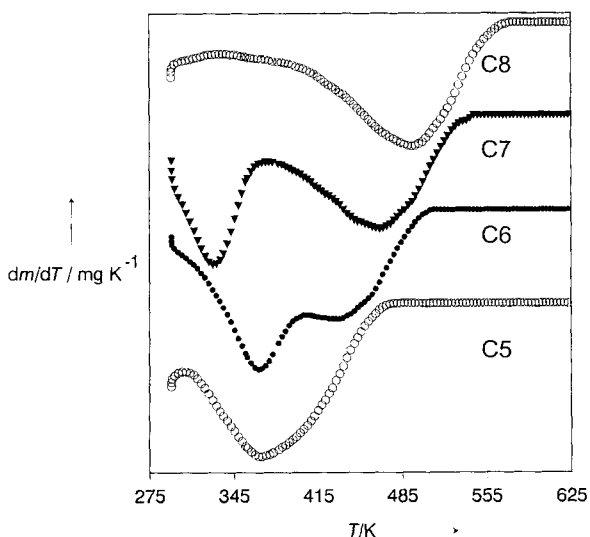


Fig. 3. Differential mass loss, dm/dT , during the TPD. The curves are separated from each other for the sake of clarity.

mass loss of the different sorbates occurred are given in Table 2. The reported results were verified by measurements on a different silicalite sample using a different heating rate (7 K min^{-1}).

Table 2. Temperatures at which the mass loss of the *n*-alkanes is at a maximum.

<i>n</i> -Alkane	T [K] of maximum mass loss	T [K] of maximum mass loss
<i>n</i> -butane	–	355
<i>n</i> -pentane	–	369
<i>n</i> -hexane	367	429
<i>n</i> -heptane	329	467
<i>n</i> -octane	–	493
<i>n</i> -nonane	–	512
<i>n</i> -decane	–	520

While *n*-butane, *n*-pentane, *n*-octane, *n*-nonane, and *n*-decane show a single desorption step, *n*-hexane and especially *n*-heptane show a two-step desorption profile. The second desorption peak of *n*-hexane and *n*-heptane, and the desorption peaks of the other *n*-alkanes occur at increasing temperatures in accordance with their increasing chain length. The first desorption peak of *n*-hexane and *n*-heptane occurs, however, at lower temperature than expected on the basis of the chain length of these two *n*-alkanes. Furthermore, it is remarkable that the first desorption step of *n*-heptane takes place at a lower temperature than that of *n*-hexane.

The results show that at high loadings some of the adsorbed *n*-hexane and *n*-heptane molecules desorb more easily from silicalite than the other *n*-alkanes. Since the first desorption step of *n*-heptane takes place before that of *n*-hexane, this first mass loss should be determined by entropic effects rather than by energetic effects. This means that the low temperature at which the first desorption peak occurs should be caused by a relative high gain in entropy upon desorption compared to the other *n*-alkanes. The relative high gain in entropy upon desorption can only be the result of a low entropy value, a constrained position of the adsorbed *n*-hexane and *n*-heptane molecules at high loadings.

The two-step desorption profile of *n*-hexane and *n*-heptane gives evidence for commensurate freezing of these two *n*-alkanes

in silicalite. The commensurate freezing of some of the molecules in the zigzag channels at high loadings results in a particularly low entropy value for these molecules. Consequently, the desorption of these *n*-hexane and *n*-heptane molecules will result in a relative high gain in entropy causing the first desorption peak to occur at relatively low temperatures. Partial desorption then allows a rearrangement of the adsorbed *n*-hexane and *n*-heptane molecules, resulting in an ordering similar to the ordering of the other *n*-alkanes with a normal entropy value. The similarity in ordering is reflected in the second desorption peak of *n*-hexane and *n*-heptane and the desorption peak of the other *n*-alkanes. These peaks occur at temperatures that are in accordance with the chain length of the *n*-alkane. The occurrence of a rearrangement during the desorption of *n*-hexane and *n*-heptane is consistent with the earlier interpretation of Richards and Rees^[8] of a two-step desorption of *n*-hexane from silicalite. The observation of a single-step desorption of the other *n*-alkanes agrees with the computational results, which indicated the absence of commensurate freezing for these molecules.

Furthermore, it can be concluded that the *n*-heptane molecules are much more constrained in the zigzag channels than the *n*-hexane molecules. This is indicated by the lower temperature of desorption, compared to that of *n*-hexane, at which the first *n*-heptane desorption peak occurs. The last result is supported by the simulated^[11] and measured^[12–5] adsorption isotherms of *n*-hexane and *n*-heptane. These show that the step in the adsorption isotherm of *n*-heptane is more pronounced than the step in the adsorption isotherm of *n*-hexane.

The temperature programmed desorption of *n*-alkanes from silicalite has provided evidence for the existence of a kind of phase transition during the filling of silicalite. Moreover, in agreement with the results from computer simulations, the occurrence of this transition is a subtle function of the *n*-alkane length and only occurs for molecules that just fit into the zigzag channels.

Received: July 7, 1995 [Z 81801E]

German version: *Angew. Chem.* 1995, 107, 2765–2767

Keywords: alkanes · catalysis · thermochemistry · zeolites

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