

Sorption kinetics of n-hexane in MFI-type zeolites investigated by micro-FTIR spectroscopy

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The sorption kinetics of n-hexane in MFI-type zeolites of different sizes have been measured by means of micro-FTIR spectroscopy. To check for an influence of the Si/Al ratio, $n_{\text{Si/Al}}$, on the sorption characteristics, a sample of silicalite was also investigated. The measured transport diffusivities show neither a dependence on the crystal size nor on the Si/Al ratio. The temperature dependence is shown to follow an Arrhenius-type law. The results of this study compare well with literature data obtained by different techniques.

1. INTRODUCTION

The pore diameters of MFI-type zeolites are comparable to the size of many commercially important molecules, such as aromatics or linear or branched hydrocarbons [1]. Thus, the study of the diffusion of reactive molecules in the channel system of zeolite catalysts is of considerable interest for the understanding of the catalyst performance. A variety of methods has been developed and applied to the measurement of diffusion coefficients, amongst others gravimetric techniques [2], neutron scattering [3], NMR [4] and Frequency Response [5]. The FTIR technique offers the possibility to study sorption and sorption kinetics under conditions close to those of catalytic experiments. By the use of an 'IR microscope', single crystals have become accessible to the FTIR technique.

In this study, we present the results of experiments performed on the sorption of n-hexane in HZSM-5 single crystals of different sizes. To examine the influence of the Si/Al ratio, $n_{\text{Si/Al}}$, on the sorption properties, a silicalite sample has additionally been studied.

2. EXPERIMENTAL SECTION

The IR technique, as developed by Karge and Niessen [6], has been applied previously to the study of sorption kinetics in the single-component systems benzene / HZSM-

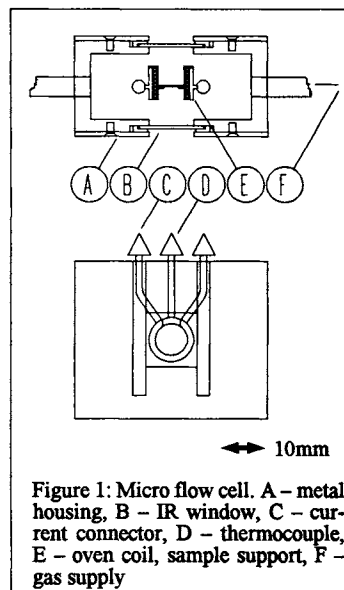


Figure 1: Micro flow cell. A - metal housing, B - IR window, C - current connector, D - thermocouple, E - oven coil, sample support, F - gas supply

5, ethylbenzene / HZSM-5 as well as to the binary systems ethylbenzene / benzene / HZSM-5 [7] and *p*-xylene / benzene/HZSM-5 [8]. The IR technique employs the time-dependent absorbance of an IR band characteristic of the sorbate molecule under consideration. By referencing the spectra to the unloaded sample, the measured extinction is only due to the sorbate absorbance.

Experimental Set-up. The experimental set-up comprises an IR spectrometer (Perkin Elmer model 1800) with attached IR microscope, gas dosing system and a flow cell.

The microscope (SpectraTech model IR-Plan) is a research-grade optical microscope modified for application in the IR spectral range. Focusing is accomplished by Cassegrainian-type mirrors. Optical and IR beam paths are collinear and switched by tilting mirrors. Thus, samples may be characterized and selected visually before recording IR spectra.

The focal diameter of the IR beam is about 0.5 mm; by adjustable rectangular apertures, the beam may be confined further to the desired sample area. Strictly speaking, the IR microscope is operated as a microscope only in optical mode, there creating a magnified image of the sample. In IR mode, the image is created at a 1:1 scale on a narrow band MCT detector with a sensitive area of about $250 \times 25 \mu\text{m}^2$.

Minimum spatial resolution is given by the diffraction limit. In the IR spectral range, approximately $10 \mu\text{m}$ may be achieved. In an uptake experiment, however, the minimum sample size is rather limited by the signal-to-noise ratio. Thus, typical areas are $40 \times 40 \mu\text{m}^2$.

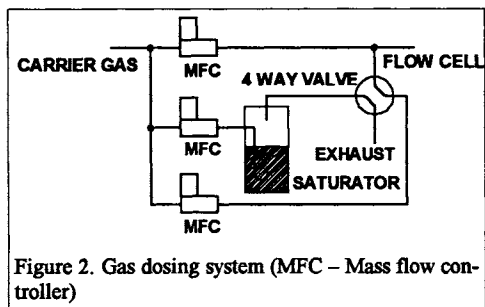


Figure 2. Gas dosing system (MFC – Mass flow controller)

Besides the possibility to study sorption kinetics in single crystals which may not be pressed into self-supporting wafers, IR microscopy requires only tiny amounts of sample, *ca.* 10^{-4} mg in comparison to 10 mg in the conventional IR technique.

The sample cell, attached to the IR microscope by means of an XY stage is a micro flow cell (See Figure 1). The cell is manufactured completely of stainless steel. Sample observation is performed through CaF_2 windows sealed with Teflon rings. The cell accommodates a micro oven, the diameter of which is about 10 mm.

Sorbates are admixed to an inert gas flow by means of a bubble saturator. The saturated gas stream is added to a large flow of inert gas, thereby adjusting the sorbate partial pressure. In Figure 2, the gas dosing system is illustrated. For the study of multi-component systems, several gas channels (mass flow controller and saturator) are combined.

Samples are deposited on a CaF_2 disc located in the center of the oven coil. After deposition and selection of the desired sample area, no further manipulation of the sample is necessary.

Table 1: Characteristics of the samples employed.

Sample	Geometry	Dimensions [μm]	$n_{\text{Si/Al}}$
A	Slab	100 x 20 x 20	96
B	Slab	60 x 13 x 13	900
C	Sphere	3.27*	30

* Equivalent radius

Activation. Activation is performed by slowly heating the sample (rate 5 K/min) from ambient temperature to 675K, keeping this temperature for 2h and subsequently lowering to the required sorption temperature at a rate of 10 K/min. During this temperature program, a carrier gas stream of 10 ml/min Helium is maintained.

Samples. Uptake experiments have been performed on two HZSM-5 samples exhibiting different sizes and crystal shapes. To study the effect of the Si/Al ratio, $n_{\text{Si/Al}}$ experiments were additionally conducted on a silicalite sample. The main characteristics of the samples employed are summarized in Table 1.

Samples A and B were kindly provided by Prof. J. Weitkamp, University of Stuttgart, Germany, sample C was granted by Degussa, Wolfgang, Germany. The crystallinity of all samples was checked by XRD. Although a good crystallinity was found in all cases, the investigation of samples A and B in polarized light showed hour-glass like structures within. This observation might indicate intracrystal interfaces as discussed by Geus *et al* [9] which influence diffusion pathways and thus the sorption behaviour.

The sorbate under investigation, n-hexane, was purchased from Fluka and was of spectroscopic grade. No additional purification was performed.

3. THEORETICAL

The measured uptake kinetics are modeled by a numerical solution of the diffusion equation

$$\frac{\partial}{\partial t} c(x, t) = D \frac{\partial^2}{\partial x^2} c(x, t)$$

assuming sorbate diffusion as the rate controlling process.

Details of the numerical procedure will be published elsewhere [10]. The sample geometry (e.g. spherical or cylindrical symmetry) is taken into account. The parameters adjusted in fitting the experimental data are (a) the transport diffusivity, D , and (b) the rate controlling mass transfer from the surrounding gas phase into the zeolite, m . The crystal size has been determined from SEM micrographs and is thus fixed.

From blank experiments, the time dependence of the sorbate concentration in the gas phase has been determined to follow an exponential law

$$c_{\text{ext}} = c_{\text{ext}}^{\text{stat}} (1 - \exp(-\beta t))$$

with the time constant $\beta \approx 0.6 \text{ s}^{-1}$.

4. RESULTS AND DISCUSSION

Absorbance Spectra. In Figures 3 and 4, spectra of the freshly activated, unloaded zeolite sample A, as well as of the otherwise unchanged sample after admitting a partial pressure of 3.1 mbar of n-hexane are given. The experimental resolution was 2 cm^{-1} . Although 25 spectra were accumulated, the signal-to-noise ratio is, due to the small sample area of about $20 \times 20 \mu\text{m}^2$, rather low. The band at 2350 cm^{-1} is attributed to CO_2 present in the beam path within the IR microscope. The spectrum of the freshly activated sample exhibits IR bands at 2007, 1882 and 1644 cm^{-1} which may be attributed to overtones of zeolite lattice vibrations [11]. The broad structure at 3500 cm^{-1} is due to SiOH groups of lattice defect sites [12]. After equilibration of the sample with 3.1 mbar of n-hexane, the positions and relative intensities of the IR

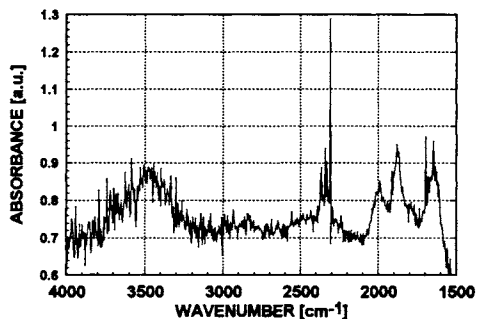


Figure 3. IR absorbance spectrum of freshly activated HZSM-5, sample A, $T=398\text{K}$, 100ml/min He gas flow.

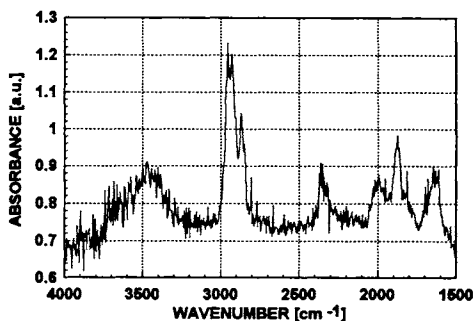


Figure 4. IR absorbance spectrum of sample A after uptake under 3.1mbar of n-hexane, conditions otherwise unchanged.

bands mentioned remain essentially unchanged. Additionally, the spectrum features the IR bands characteristic of n-hexane, i.e., the asymmetric vibrations of the CH_3 - and CH_2 -groups at $\nu=2960, 2930\text{ cm}^{-1}$, respectively and the symmetric counterparts at $2890, 2870\text{ cm}^{-1}$.

Thus, by referencing the absorbances of the loaded samples to those of the corresponding unloaded samples, any influence of the sample itself on the IR absorbance is eliminated and the amount of sorbate may be deduced simply from the intensity of the characteristic IR bands. In the case of n-hexane, the asymmetric vibration of the methyl group, $\delta_a^{\text{CH}_3}$, is evaluated.

Uptake spectra. In Figures 5, 6 and 7, the uptake curves for samples A, B and C, respectively, are presented. Symbols denote experimental data, the corresponding calculated uptake curves are plotted with solid lines. To illustrate the quality of the data, no accumulation and/or averaging of the absorbance calculated has been performed. However, repeated uptake runs

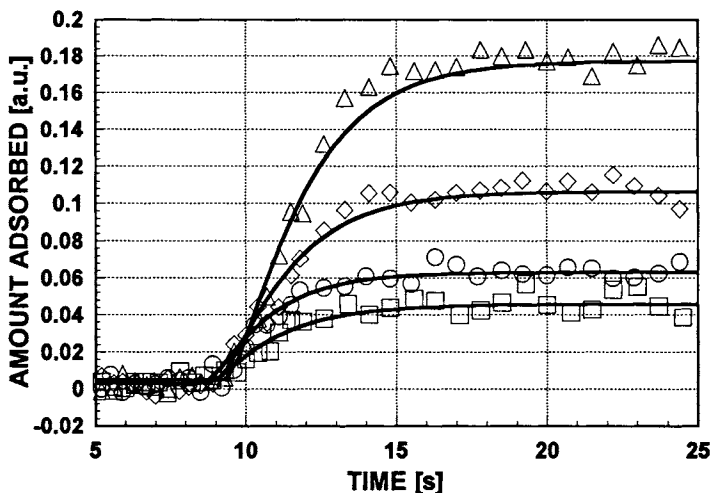


Figure 5. Uptake under 3.1 mbar of n-hexane in HZSM-5, sample A at various sorption temperatures. Solid lines: calculated uptake curves, symbols: Δ – 398 K , \diamond – 423 K , \circ – 448 K and \square – 473 K .

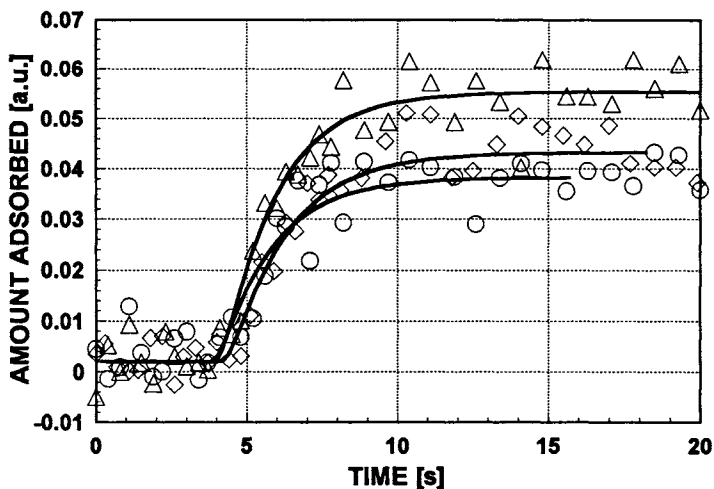


Figure 6. Uptake under 3.1 mbar of n-hexane in HZSM-5, sample B at various sorption temperatures. Solid lines: calculated uptake curves, symbols: Δ – 398 K, \diamond – 423 K and \circ – 448 K.

may be performed in order to reduce the experimental error. Since the amount of sorbate decreases with increasing temperature, the signal-to-noise ratio deteriorates in the uptake runs performed at higher temperatures.

In order to determine the activation energy of the diffusion, the uptake experiments were conducted at temperatures in the range 398 to 473 K. In Table 2, results are compiled. The errors of the transport diffusion coefficient are estimated to be $\pm 0.75 \cdot 10^{-8}$ cm²/s. A thermodynamic correction [13] of the transport diffusivity has not been applied. However, since the

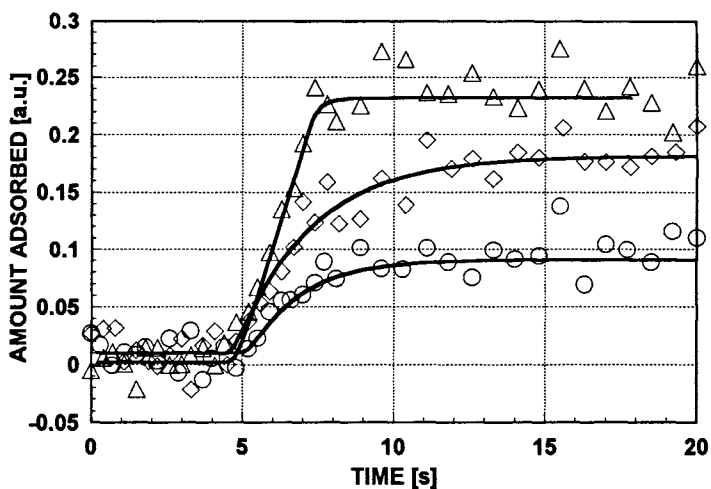


Figure 7. Uptake under 3.1 mbar of n-hexane in HZSM-5, sample C at various sorption temperatures. Solid lines: calculated uptake curves, symbols: Δ – 398 K, \diamond – 423 K and \circ – 448 K.

Table 2. Temperature dependence of transport diffusivities.

Sample	Temperature [K]	Transport diffusivity [10^{-8} cm ² /s]
A	398	4.5
	423	4.3
	448	8.0
	473	9.5
B	398	4.8
	423	5.5
	448	6.0
C	398	1.5
	423	2.0
	448	2.3

partial pressure step applied is rather small, the correction will be close to unity.

The uptake steps were followed by desorption until the sorbate was completely removed. The diffusivities calculated from the desorption kinetics were the same as in the uptake steps.

To check for possible hysteresis effects as observed by Beschmann *et al.* [14] in the sorption of *p*-xylene in HZSM-5, each uptake step was repeated at least two times. However, no indication for hysteresis effects was found.

The results described in this report compare well with data of Van-Den-Begin *et al.* [15] obtained on silicalite samples with an equivalent radius of 31 μm by means of Single-Step Frequency-Response. The authors report a self diffusion coefficient for n-hexane of about $2 \cdot 10^{-8}$ cm²/s at a temperature of 444 K. However, it has to be considered that, due to the shape of the sorption isotherm, the self-diffusion coefficient will be somewhat smaller than the transport diffusion coefficient. Caro *et al.* [16] report a transport diffusion coefficient of $1.8 \cdot 10^{-7}$ cm²/s for the system n-hexane/HZSM-5 at 298 K, determined gravimetrically. The crystals used in that study were of prismatic shape, the dimensions being 330 μm (z-axis), 110 μm

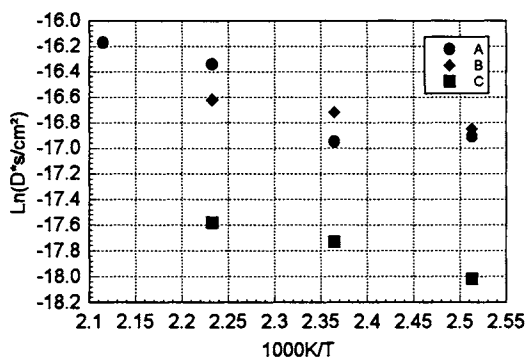


Figure 8. Arrhenius plot of transport diffusivities in samples A (●), B (◆), and C (■)

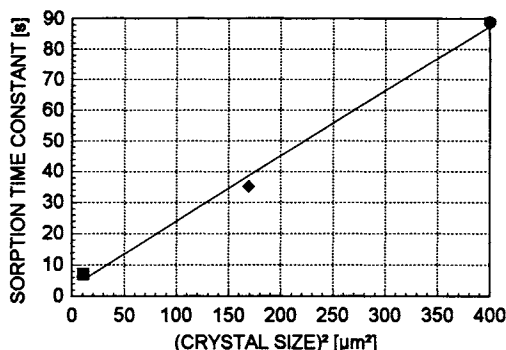


Figure 9. Time constant of sorption, τ , at 398 K vs. square of crystal dimension, R^2 for samples A, B and C (symbols as in Figure 8).

(x/y-axis). The diffusivity obtained is larger by a factor of 5 compared to our results.

Temperature Dependence. Assuming an Arrhenius law for the temperature dependence, the activation energy for the diffusion process was calculated. The results are compiled in Figure 8 as well as Table 3. The difference of activation energies between samples A and B may be attributed to the different ratios $n_{Si/Al}$ (30 and 900, respectively). The activation energy obtained here compares well with a value of 17 ± 4 kJ/mol as obtained by Van-den-Begin *et al.* [15].

Table 3. Activation energy for diffusion of n-hexane in samples A, B and C.

Sample	Activation energy [kJ/mol]
A	15.6
B	6.6
C	12.6

Si/Al ratio. As can be seen from the data compiled in Table 2, the transport diffusivities in sample A (HZSM-5) and B (silicalite) are virtually the same. Since the sorbate molecule is nonpolar, it does not exhibit a large interaction with acid centres present in sample A. To prove this, comparative studies with olefins will be presented in a later report.

Size dependence. Provided that the sorption process is determined by diffusion of the sorbate in the channel system of the sorbent, the time constant for the uptake process, τ , defined as

$$\tau = \frac{R^2}{D}$$

should depend linearly on the square of the crystal dimension, R [17]. To prove this relation, Figure 9 presents a plot of τ vs. R^2 . A linear relation is clearly observed. This behaviour coincides with the findings of Voogd *et al.* [18] who investigated the uptake of n-hexane in HZSM-5 crystals by means of a constant volume-variable pressure system.

5. CONCLUSIONS

In this study, uptake kinetics have been investigated for the system n-hexane/HZSM-5 by means of *micro*-FTIR, an extension of the 'conventional' FTIR technique. We would like to summarize the major features of this technique as follows:

- Direct, i.e., *in-situ* observation of the sorbate within the channel network of the zeolite,
- Study of sorption in a temperature regime close to that of catalytic experiments,
- No 'bed-effects' due to intercrystalline diffusion of sorbate,
- Due to large carrier gas flow, experiments are performed under isothermal conditions.

The transport diffusivities determined are of the order of $4 \cdot 10^{-8}$ cm²/s, which corresponds well to literature data obtained by various other techniques. The activation energy for the diffusion process has been found to be 6-15 kJ/mol.

The uptake time-constant depends linearly on the square of the crystal size, indicating diffusion as the dominant step in rate control. Uptake kinetics are well described by a model taking into account only diffusion without rate-controlling steps superimposed, such as surface barriers [19] or thermal effects [20].

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