

# Diffusion in zeolites: is surface resistance a critical parameter?

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**Abstract** Gravimetric uptake measurements were performed with cyclohexane for different Silicalite-1 crystals sizes. It was observed that the apparent diffusion coefficients vary with crystal size, confirming the existence of a surface resistance. Considering that surface and the intracrystalline characteristic diffusion times are additives, it was possible to dissociate the two resistances.

Surface mass transfer coefficient was found to be in the same order of magnitude for the different samples and activated with temperature. The contribution of surface resistance to mass transfer limitation is lower at high temperatures and for the bigger crystals. Surface resistance is far from being negligible for the smaller crystals: for crystals of 2  $\mu\text{m}$ , surface resistance represents more than 60% of the total mass transfer resistance at 398 K. And crystals of that size (in the order of 2  $\mu\text{m}$ ) are usually used industrially, in order to minimize mass transfer resistance.

The surface of one of our sample was purified by etching with a solution of hydrogen fluoride, without any enhancement of the adsorption kinetic. Surface resistance may not be located at the extreme surface of the crystals but in a layer of non negligible thickness of distorted crystal structure around the crystals.

**Keywords** Diffusion · Surface resistance · Cyclohexane · Silicalite

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## 1 Introduction

Intracrystalline diffusivity is a key parameter for the design of adsorption industrial processes. However, diffusion coefficients obtained in the literature for the same adsorbate/adsorbent system can vary by several orders of magnitude. One of the hypothesis suggested in literature is the existence of a resistance to mass transfer at the crystal surface.

This barrier was first detected by macroscopic methods. Bülow et al. (1980) measured uptake curves of n-hexane in MgA zeolites and were able to dissociate intracrystalline and surface resistance from experiments with different crystal sizes. Micke et al. (1994) showed that the uptake curves of p-ethyltoluene in Na, H-ZSM-5 cannot be correctly modeled without taking into account a surface barrier. After etching the surface of ZSM-5 crystals with fluorhydric acid, Wloch (2003) recorded an important increase of the mass transfer rate, thus confirming the existence of a surface barrier.

It is with the advent of microscopic methods that the surface barrier has become indisputable. Using PFG NMR, Krutyeva et al. (2007) showed that surface resistance is not negligible for methane and ethane diffusion in NaCaA. Some of the microscopic methods even enable a direct observation of the concentration profiles inside a single crystal. Tzoulaki et al. (2008a, 2008b) measured concentration profiles of 2-methylbutane and 2-methylpropane in silicalite with interference microscopy and concluded on the absence of surface resistance. On the contrary, Zhang et al. (2009) showed by infrared microscopy that the concentration profiles of n-hexane in crystals of mordenite is essentially flat, proving that the surface contributes to more than 90% of the total mass transfer resistance.

These results show that there is still a need for a better comprehension of surface resistance, because very few is

**Table 1** Samples synthesis conditions

Sample	Silicium source	SiO <sub>2</sub> (mole)	TPAOH (mole)	TPABr (mole)	NaOH (mole)	Benzene-1,2-diol (mole)	H <sub>2</sub> O (mole)	Temp. (°C)	Duration (day)
1	Aerosil 130	60	20	20	–	–	1500	170	2
2	TEOS	25	9	–	–	–	9480	80	4
3	Aerosil 130	60	20	20	–	–	2000	170	2
4	Aerosil 130	60	20	20	–	–	1500	170	2
5	Ludox HS40	60	–	20	10	–	2000	175	2
6	Aerosil 130	60	–	12	15	24	1800	160	7

known concerning its origin, the adsorbate/adsorbent systems concerned, the influence of operating conditions (such as temperature and pressure) and the influence of crystals synthesis methods.

The aim of this work is to contribute to a better understanding of this phenomena, by evaluating the surface mass transfer resistance of cyclohexane in Silicalite-1 for different crystals, temperatures and adsorbate partial pressures.

## 2 Experimental section

### 2.1 Sample preparation

**Crystals synthesis** The synthesis conditions, summarized in Table 1, were chosen so as to obtain crystals with different radii but with the same morphology, i.e. nearly spherical. As it is impossible to obtain a large range of crystals sizes with the same synthesis conditions, different reactions had to be employed.

A TPA-silicalite precursor sol was prepared by hydrolyzing Silicon source with a structuring agent in water at room temperature. The sol was aged at room temperature for at least 24 h before heating, except for the sample 6. To obtain bigger crystals, the number of nuclei has to be reduced, so the sol was not aged and a complexing agent, benzene-1,2-diol (Shao et al. 2000), was used. The hydrolyzed solution was filtered through a filter membrane (nominal pore size 0.22 µm) before analysis by BET, SEM and XRD.

The template was removed by calcination in air at 823 K for 12 H.

**Crystals etching** One of our as-synthesized material (sample 3) was etched with a solution of hydrogen fluoride. The experimental conditions are the same as related by Wloch (2003), except for the HF concentration which is higher in our case ( $\approx \times 3$ ). The etching of the non-calcined zeolite was performed in a Teflon container into which 1 g of zeolite and 11 cm<sup>3</sup> of acetone were introduced. After the add of 0.565 g of HF at 40%, the mixture was stirred for 3 and 6 minutes.

**Table 2** Samples characterization

Sample	Microporous volume (cm <sup>3</sup> /g)	Radius (µm)
1	0.19	0.34
2	0.18	0.41
3	0.15	1
4	0.19	2
5	0.17	10.2
6	0.18	17

Then, the mixture was immediately diluted in an important volume of water and filtered quickly through a polypropylene membrane. The crystals were further washed with two liters of distilled water during the filtering process, and then dried and calcined in air.

### 2.2 Characterization

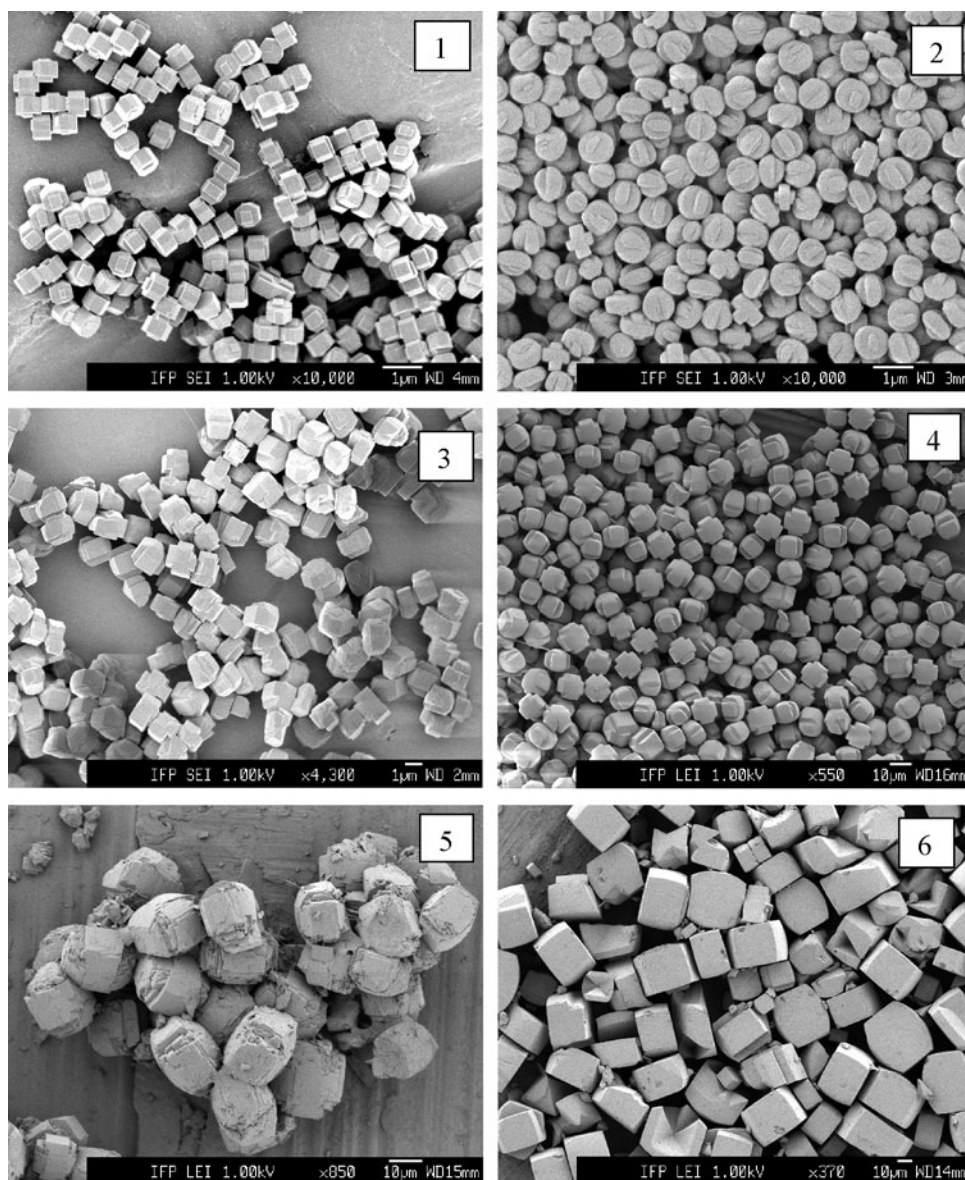
X-ray diffraction (XRD) patterns were collected with a Bruker AXS D4 Andeavor between  $2\theta = 2$ –60. Crystallinity was determined using a highly crystalline Silicalite-1 sample. No amorphous silica was found in our samples.

Microporous volumes were recorded using a Micromeritics ASAP 2000 series volumetric unit. As can be seen in Table 2, the microporous volumes are constant for all samples (around 0.18 cm<sup>3</sup>/g). The zeolite samples were also characterized by scanning electron microscopy using a Jeol scanning microscope model JSM6340 and crystals sizes were determined by picture analysis. Pictures of the crystals, shown on Fig. 1, show that all the samples have nearly the same spherical morphology.

### 2.3 Kinetic measurements

Gravimetric uptake measurements were performed on a Setaram thermogravimetric balance used with a sorption module (see Fig. 2). Sorbate partial pressures were adjusted by bubbling the inert gas (helium) in a saturator. The mass of

**Fig. 1** SEM pictures of the different samples: (1: 0.34  $\mu\text{m}$ ; 2: 0.41  $\mu\text{m}$ ; 3: 1  $\mu\text{m}$ ; 4: 2  $\mu\text{m}$ ; 5: 10.2  $\mu\text{m}$ ; 6: 17  $\mu\text{m}$ )



silicalite introduced into the balance was always kept very small ( $\sim 25$  mg) in order to minimize the intrusion of extracrystalline resistances. Prior to experiment, the sample temperature was raised at a uniform rate of 10 K/min from ambient to 573 K in dry helium at a rate of 3 NL/h for 5 hours to remove residual water. Then temperature was reduced at the rate of 10 K/min and stabilized for sorption. Temperature is adjusted for each sample, to ensure that mass transfer is the limiting step and to limit the global experiment time. Furthermore, experiments were done at low adsorbate partial pressure (1.6–5 mbar) to reduce thermal effects. Cyclohexane was obtained from Sigma Aldrich, with specified purity over 99.8%, and was used without further purification.

### 3 Theory

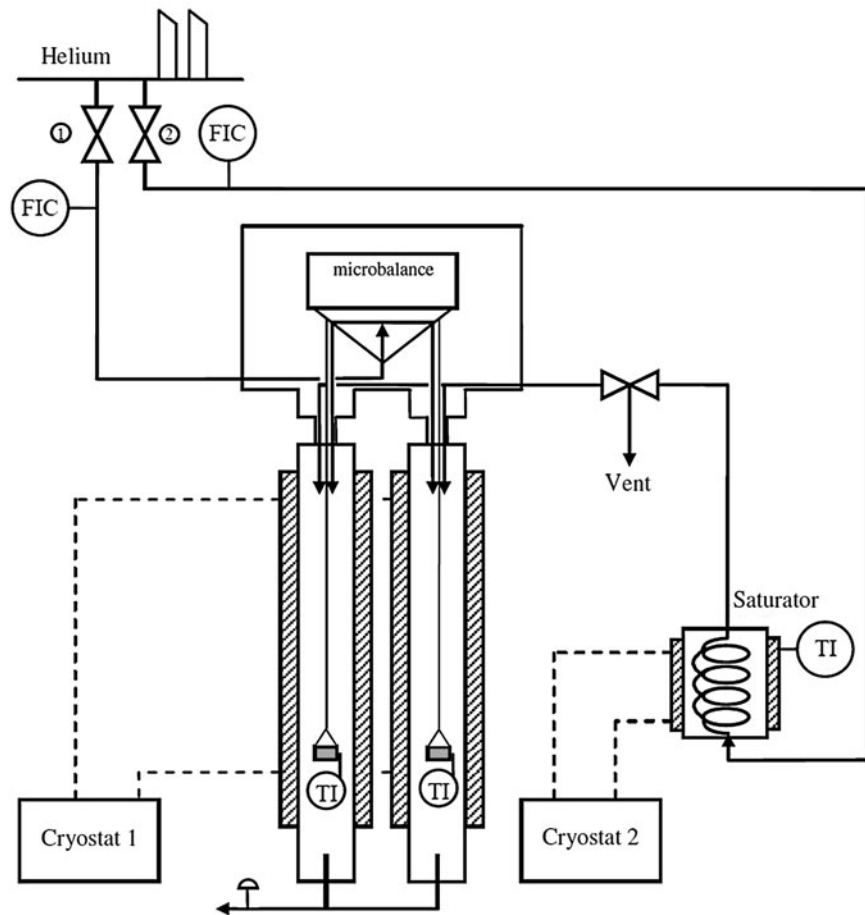
In order to evaluate the mass transfer coefficients, a model of the uptake curve has to be established.

#### 3.1 Model assumptions

The main assumptions of the model are:

1. No temperature variation (the whole system is isothermal).
2. Isotherms follow a langmuirian behaviour.
3. The evolution of the effective or corrected diffusivity  $D_c$  with adsorbed phase concentration can be represented by Darken's equation.

**Fig. 2** Thermogravimetric experimental setup



Other hypotheses are:

4. Crystals are spherical of radius  $r_c$ .
5. Extracrystalline resistance is negligible. The concentration in the fluid phase around the crystals is constant and equal to the fluid phase concentration. As will be shown later on, this assumption has been validated by comparing uptake curves with different sample masses.
6. Intracrystalline diffusivity follows Arrhenius' law and is the same for all silicalite crystals.
7. Surface resistance is represented by the solid film model (Karger and Ruthven 1992).

### 3.2 Model equations

When all these conditions are fulfilled, the equations of the model are:

- In the crystal:

$$\frac{\partial q}{\partial t} = \frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left( r^2 \cdot \frac{D_0}{1 - \lambda} \cdot \frac{\partial q}{\partial r} \right) \quad (1)$$

with:

$q$ : adsorbed phase concentration (g/g)

$r$ : radial crystal coordinate (m) ( $0 \leq r \leq r_c$ )

$D_0$ : intracrystalline self-diffusivity ( $\text{m}^2 \cdot \text{s}^{-1}$ )

$\lambda$ : fractional saturation ( $\lambda = \frac{q}{q_s}$ )

- In the centre of the crystal:

$$\left. \frac{\partial q}{\partial r} \right|_{r=0} = 0 \quad (2)$$

- At the surface of the crystal:

$$-\frac{D_0}{1 - \lambda} \cdot \left. \frac{\partial q}{\partial r} \right|_{r=r_c} = k_s \cdot (q^* - q|_{r=r_c}) \quad (3)$$

$q^*$  is the adsorbed phase concentration in equilibrium with the fluid phase:

$$q^* = q_s \cdot \frac{b \cdot C}{1 + b \cdot C} \quad (4)$$

### 3.3 Method of solution

Equations (1) to (4) were reduced to a set of algebraic and ordinary differential equations using the finite difference method. These equations were then numerically integrated using the IMSL DASPG routine, based on Petzold-Gear's integration method.

### 3.4 Model simplification

A first tentative to fit the experimental uptake curves with the complete model was finally abandoned. Indeed, the short-time region of the curves is much more subject to experimental incertitude than the long-time region. In particular, the initial step of the bulk-gas adsorbate concentration is dispersed, inducing a sigmoidal shape for the uptake curve. This dispersion is dependent on different experimental conditions (flow rates, temperature) and is very difficult to take into account. Moreover, a systematic numerical parameter estimation procedure is very time consuming.

It was therefore decided to concentrate on the long time region of the curves. The equations were simplified by supposing that the characteristic diffusion times are linearly additive:

$$t_{diff} = \frac{r_c^2}{\pi^2 D_c} + \frac{r_c}{3k_s} = \frac{r_c^2}{\pi^2 D} \quad (5)$$

where  $D$  is an apparent global diffusion coefficient.

The variation of the effective diffusivity  $D_c$  with the adsorbed phase concentration was taken into account using the correlation established by Garg and Ruthven (1972) for a langmuirian adsorption.

In that case, the expression for the uptake curve is:

$$\begin{aligned} \frac{m_t}{m_\infty} &= 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 t}{t_{diff}}\right) \\ &= 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{\pi^2 D t}{r_c^2}\right) \end{aligned} \quad (6)$$

In the long time region, all terms except the first in the series of exponential terms become negligible so that the uptake

curve approaches the asymptotic form (Karger and Ruthven 1992):

$$\frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2} \exp\left(-\frac{t}{t_{diff}}\right) \quad (7)$$

By plotting  $\ln(1 - \frac{m_t}{m_\infty})$  versus time, the solution will approach a straight line in the long time region, and the slope of this line yields directly the global characteristic diffusion time (or the apparent diffusion coefficient).

To verify the assumption represented by (5), the slope of the long time domain solutions of (6) was compared to the slope obtained with the complete model for a whole range of parameters. Results can be seen on Fig. 3. The X-axis of this figure is the ratio between the two characteristic diffusion times:

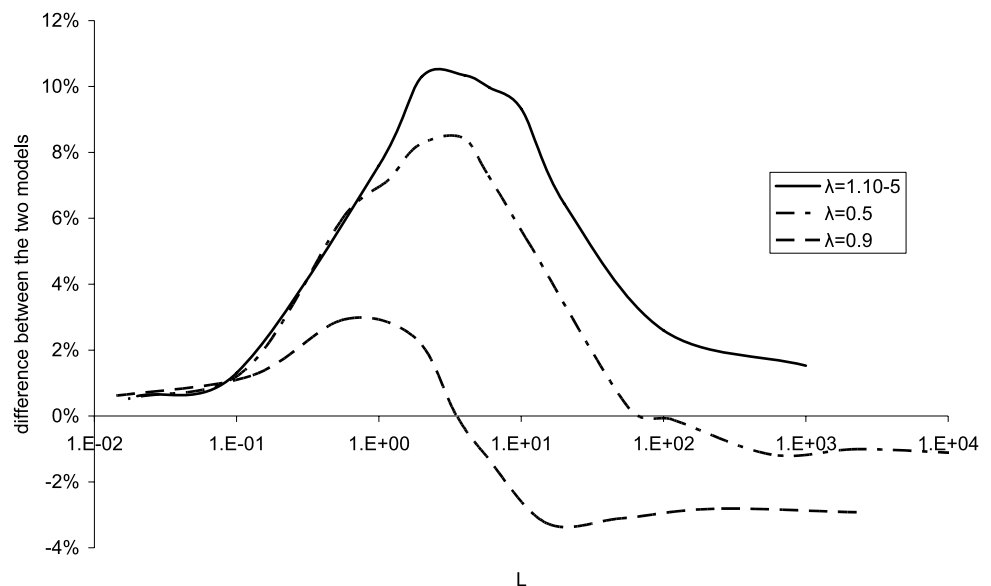
$$L = \frac{k_s \cdot r_c}{D_c} \quad (8)$$

The difference between the two models is always below 10% (the maximum is of course in the case when surface and intracrystalline resistances characteristic times are in the same order of magnitude). It is interesting to note that the error is not accentuated at higher saturation loadings. This validates the use of the correlation of Garg and Ruthven (1972) to correct the effective diffusivity from the adsorbed phase concentration effect.

This maximal error of 10% was considered to be acceptable. Consequently, the experimental uptake curves have been exploited using (7).

Using this methodology, the global diffusion time  $t_{diff}$  can be estimated for each uptake curve. If all the crystals can be tested at the same temperature, the variation of  $t_{diff}$  with the crystals radius enables to directly estimate  $D_c$  and

**Fig. 3** Difference between the two models as a function of  $L$  (as defined in (8) and fractional saturation  $\lambda$ )



$k_s$  at that given temperature (using (5)). However, it is not possible in practice, because at the same temperature,  $t_{diff}$  varies by several orders of magnitude for the different samples due to a large range of radii. The experimental setup is not precise enough when uptake curves reach equilibrium in less than a few minutes or more than about a day. If equilibrium time is too short, the curve may be influenced by extragranular resistances or thermal effects. On the contrary, if equilibrium time is too long, the curve can be corrupted by a very slow drift of the signal.

Consequently, the temperatures had to be adapted to the crystals sizes: the largest crystals were studied at high temperatures (408–498 K), whereas the smallest ones were studied at lower temperatures (323–398 K). It is therefore not possible to directly estimate the mass transfer coefficients from (5).

It is however possible to circumvent this difficulty by carrying out experiments in conditions where one of the mass transfer resistance is negligible. For example, only the intracrystalline mass transfer resistance is significant for very large crystals.  $D_c$  can then be estimated from the experiments with large crystals, and  $k_s$  can then be calculated from the characteristic global diffusion time of the other samples using (5). This method was adopted in this study.

**Note** If surface diffusion is neglected whereas it shouldn't be, then:

- the estimated intracrystalline diffusion coefficient will be underestimated,
- an apparent variation of the intracrystalline diffusion coefficient with crystal size should be visible.

It is therefore very useful to systematically check that there is no influence of crystal radius on diffusion coefficients measurements.

## 4 Results and discussion

### 4.1 Isotherms

The adsorption isotherms for cyclohexane in Silicalite-1 are presented on Fig. 4. It can be seen that the experimental points are very well fitted by the Langmuir model. The resulting parameters are:

$$q_s = 4 \text{ molec./u.c.}$$

$$b_0 = 4.5 \cdot 10^{-11} \text{ Pa}^{-1}$$

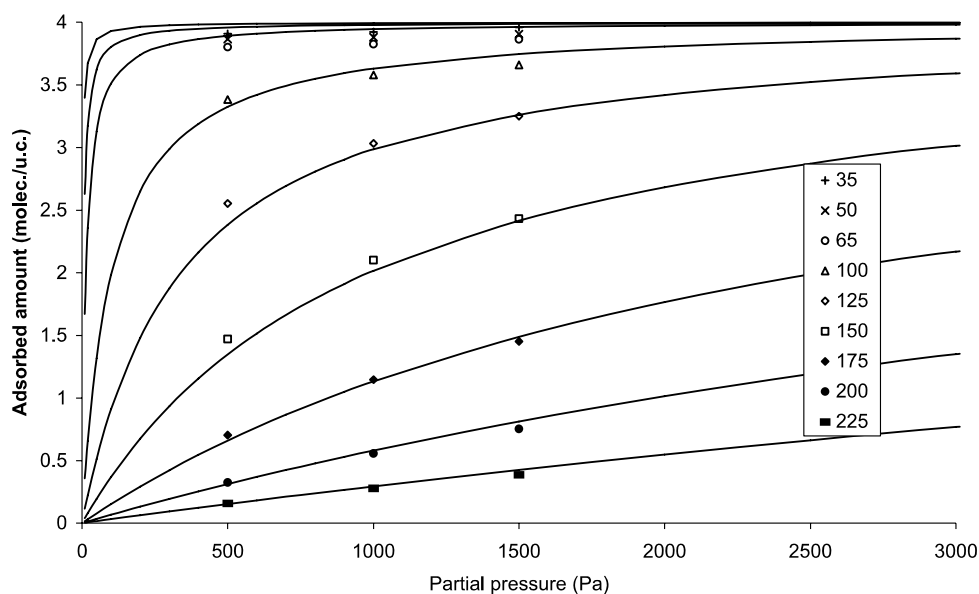
$$\Delta H = -59.5 \text{ kJ}\cdot\text{mol}^{-1}$$

Our results are globally in agreement with literature results. As can be seen in Table 4, this work's heat of adsorption is very close to the values obtained in different studies. The quantity adsorbed at saturation is coherent with the theoretical value of 4 molecules/cell, corresponding to the silicalite channels intersection sites.

**Table 3** Intracrystalline diffusion parameters (Wu et al. 1983; Ban et al. 2005; Xiao and Wei 1992; Chon and Park 1988; Cavalcante and Ruthven 1995b)

	$D_0^*$ (m <sup>2</sup> /s)	$E_a$ (kJ/mol)
This study	$6.91 \cdot 10^{-9}$	56.6
Wu et al.	$6.67 \cdot 10^{-11}$	33.8
Ban et al.	$0.20 \cdot 10^{-11}$	26.4
Xiao et al.	–	64.8
Chon et al.	$4.47 \cdot 10^{-10}$	50.6
Cavalcante et al.	–	53.5

**Fig. 4** Isotherms of cyclohexane on Silicalite-1 (points: experimental data; lines: fitted Langmuir model)



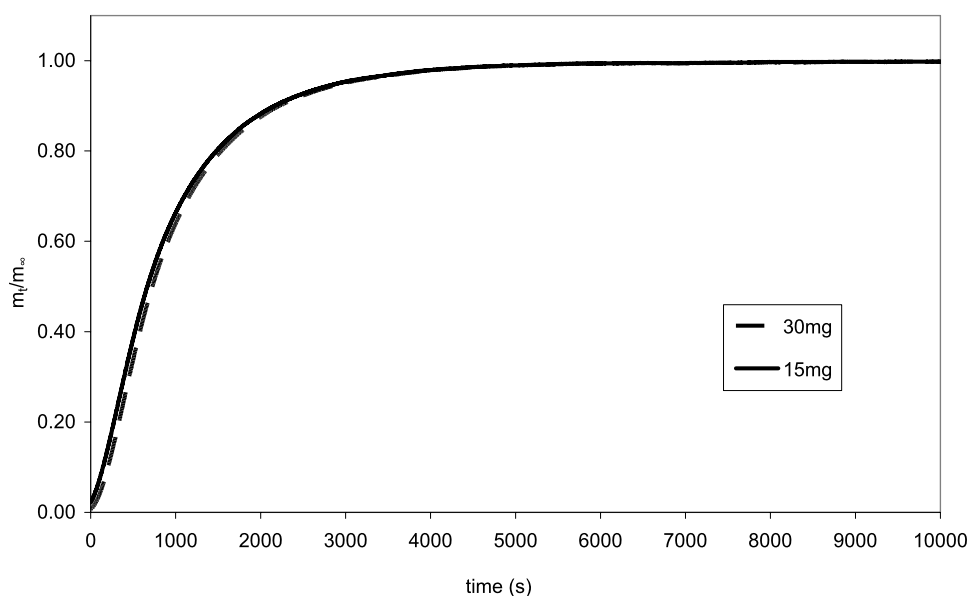
## 4.2 Influence of the mass of sample

Two uptake curves were measured in the same experimental conditions (sample 1,  $T = 348$  K, cyclohexane partial pres-

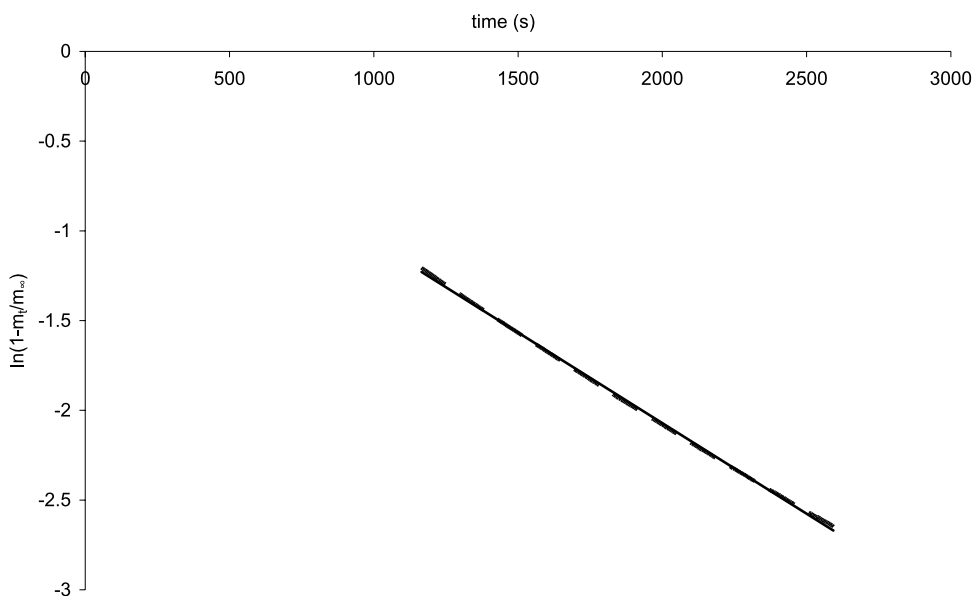
**Table 4** Heats of adsorption of cyclohexane on Silicalite-1 (Cavalcante and Ruthven 1995a; Gupta et al. 2000; Fox et al. 2004)

	$\Delta H$ (kJ/mol)
This study	−59.5
Cavalcante et al.	−63.1
Gupta et al.	−57.1
Fox et al.	−61.8

**Fig. 5** Uptake curves for sample 1 at 348 K for 2 different masses (*dotted* 30 mg, *full* 15 mg)



**Fig. 6** “Long time region” plot of the uptake curve of Fig. 5



sure of 160 Pa) except for the mass of the sample, which was varied from 15 mg to 30 mg. The two uptake curves are very close, as can be seen on Fig. 5. The model assumptions (no extracrystalline resistance and isothermal system) are therefore validated.

Figure 6 shows the corresponding “long time region” plot. The plot is linear and therefore in accordance with (7).

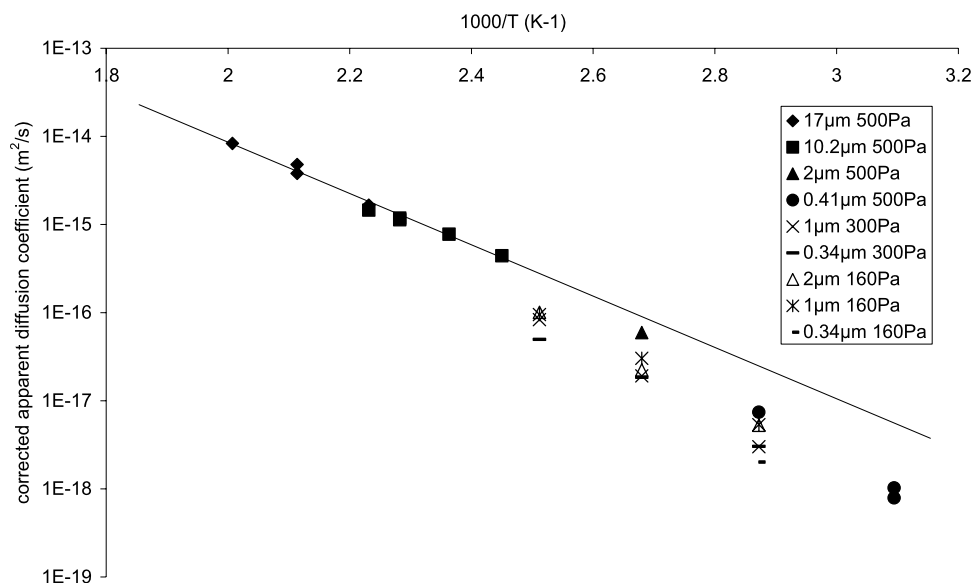
## 4.3 Estimation of the surface resistance

Apparent diffusion coefficients as a function of temperature for the different samples can be seen in Fig. 7.

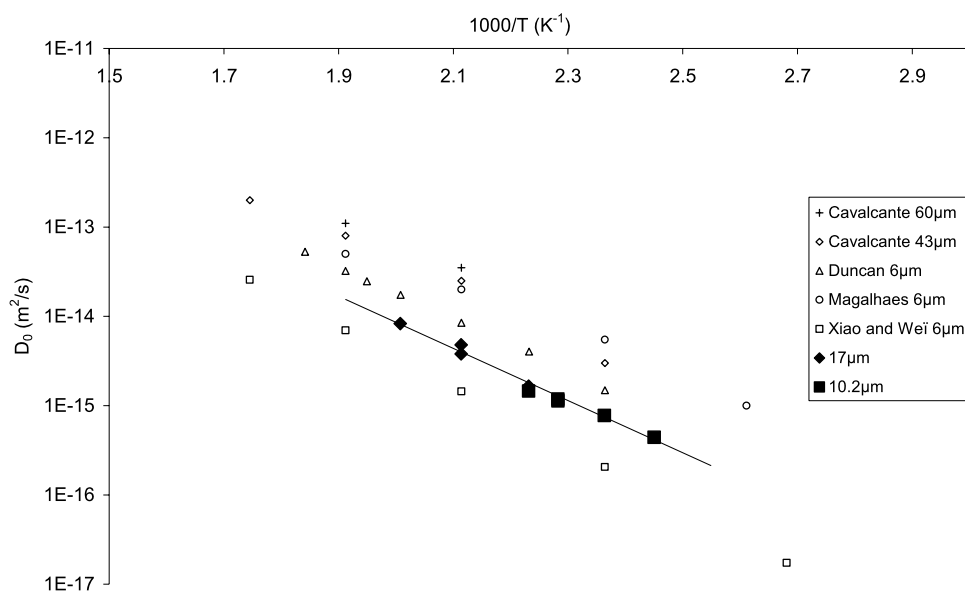
First of all, it appears clearly that apparent diffusion coefficients are not independent of crystal size. The apparent



**Fig. 7** Corrected apparent diffusion coefficient as a function of temperature for the different crystal sizes



**Fig. 8** Intracrystalline diffusion coefficient as a function of temperature compared to literature data (Cavalcante and Ruthven 1995b; Duncan and Moller 2000; Magalhaes et al. 1998; Xiao and Wei 1992)



diffusion coefficients for the smaller crystals are about an order of magnitude smaller than that of the larger crystals. Surface resistance is therefore not negligible in these conditions.

On the contrary, for temperatures comprised between 398 and 498 K (respectively  $1000/T = 2.51$  and 2), the apparent diffusion coefficients for the largest crystals are coherent and very well aligned. Surface resistance is thus negligible in these conditions. The intracrystalline diffusion coefficient of cyclohexane can therefore be directly deduced from the apparent diffusion coefficients for the larger crystals.

The results are compared to literature values on Fig. 8. It can be seen that our results are coherent with other literature studies (only diffusion coefficients measured with crystals larger than 6  $\mu\text{m}$  are shown here). The calculated pre-

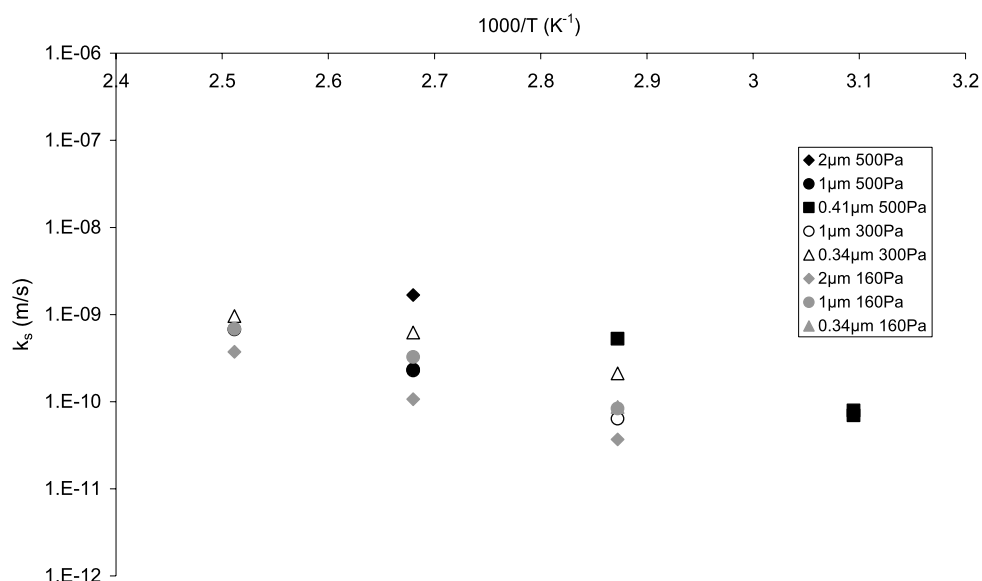
exponential factor  $D_0^*$  and activation energy  $E_a$  are listed in Table 3. The activation energy is also in agreement with other literature results (but the literature values are quite different depending on the studies).

Now that  $D_c$  can be estimated for any temperature, it is possible to calculate the values of  $k_s$  for each experiment where surface resistance is not negligible (for the smallest crystals). The resulting values of  $k_s$  are plotted on Fig. 9.

It can be seen that the values of  $k_s$  are in the same order of magnitude for the different samples. However, the values of  $k_s$  are not exactly the same for all crystals. It is possible that the nature of the surface is partly dependent of the crystal synthesis conditions. Moreover,  $k_s$  seems to be smaller at low gas phase partial pressures, although the precision of the data do not permit to conclude definitely on this point. Fi-



**Fig. 9** Surface mass transfer coefficients as a function of temperature and partial pressure



nally, mass transfer at the surface seems to be activated: one can observe a large increase of parameter  $k_s$  for the higher temperatures. The activation energy was not estimated from our experimental values, because the derived value of the activation energy is very sensitive to any uncertainty in the slope of the plot, and a great quantity of precise experimental measurements are therefore necessary to determinate the activation energy with accuracy.

Different hypothesis can explain the activated nature of  $k_s$ :

- If surface resistance is due to a distortion of the crystal structure of the surface, i.e. diffusion in the first layers of the crystal is much slower than in the interior of the crystal, then surface resistance occurs when the molecules are already in the adsorbed state. In that case, the strong molecules/adsorbent interactions would explain the activated nature of surface resistance.
- If surface resistance is due to a partial blockage of the pores at the surface, i.e. the molecules cannot penetrate into the crystalline network, then the surface diffusion kinetic depends on the adsorption isotherm. In that case, the fluid film model is more accurate (Karger and Ruthven 1992).

In an attempt to see which hypothesis is more applicable to our system, the surface of one of our samples was purified by etching the crystals surface with an aqueous-acetone solution of hydrogen fluoride, as described by Wloch (2003).

The etching was operated on sample 3, in the conditions described in the experimental section. Next, uptake curves were recorded for the original and purified crystals. The resulting uptake curves, plotted on Fig. 10, do not show any significant evolution. The apparent diffusion co-

efficients vary between  $4.2 \cdot 10^{-17}$  and  $5.8 \cdot 10^{-17}$ , which is in the order of magnitude of our experimental uncertainty. Our results are therefore different from those of Wloch (2003), who found apparent diffusivities for their etched zeolites higher than that of their regular crystals by two orders of magnitude. This is all the more surprising since Wloch (2003) used crystals much larger than ours ( $54 \times 54 \times 137 \mu\text{m}^3$ ) and a HF solution less concentrated than the one used in this study. Obviously, the origin of surface resistance is different on our crystals. The hypothesis of a non-negligible layer of distorted crystal structure around the crystals seems more probable.

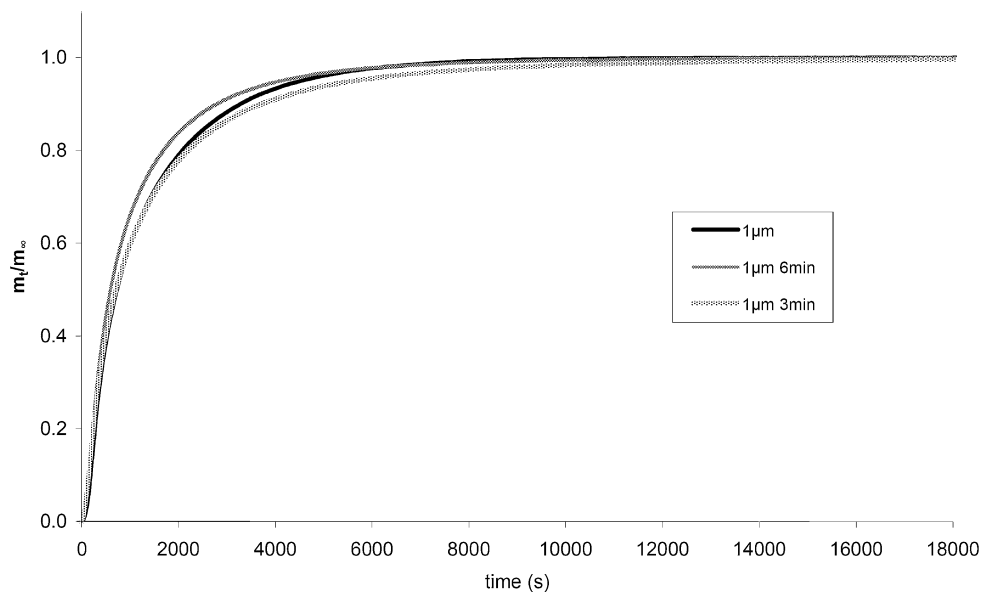
It is possible that surface resistance depends on the crystal synthesis method. As a matter of fact, Chmelik et al. (2007) also found no effect of HF etching on isobutane diffusion in crystals of Silicalite-1.

It is also interesting to evaluate the relative contribution of the two resistances as a function of the crystal size and of the temperature. Figure 11 presents the results at 348 K for different crystals sizes and Fig. 12 for the same size (2  $\mu\text{m}$ ) for different temperatures (the cyclohexane partial pressure is of 160 Pa for both figures).

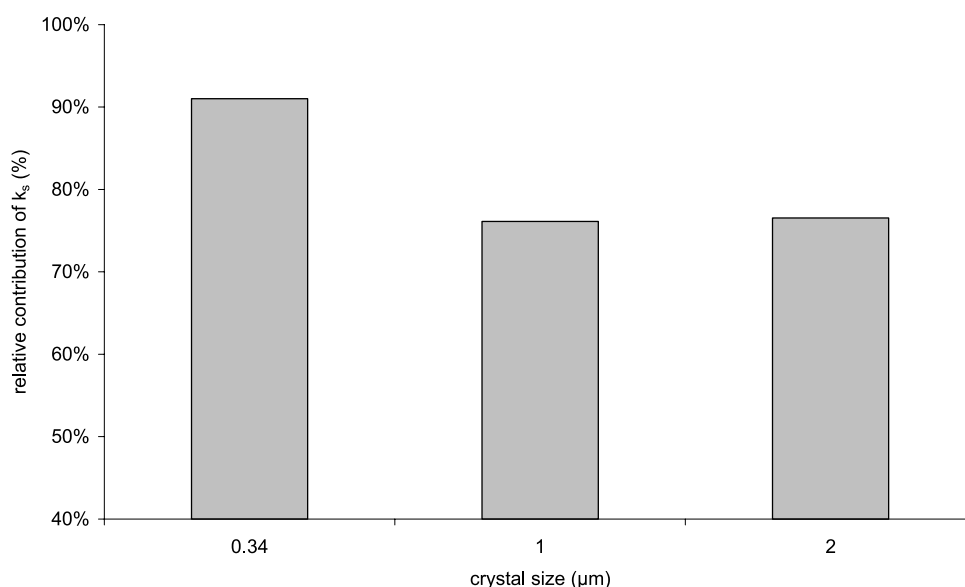
As expected, the contribution of surface resistance to mass transfer is lower at higher temperature and for the bigger crystals. Surface resistance is far from being negligible for the smaller crystals: for crystals of 2  $\mu\text{m}$ , surface resistance represents more than 60% of the total resistance at 398 K. And crystals of that size (in the order of 2  $\mu\text{m}$ ) are usually used industrially, in order to minimize mass transfer resistance.

A precise measurement of surface resistance is therefore interesting not only in a theoretical point of view, but also for a better optimization of the sizes of the crystals used in

**Fig. 10** Uptake curves of cyclohexane at 373 K and 500 Pa on sample 3 [non-etched (*black line*), 3 min etched (*dark grey line*) and 6 min (*grey line*)]



**Fig. 11** Relative contribution of  $k_s$  as a function of crystal size at 348 K and 160 Pa



industrial processes. Extrapolation of diffusion coefficients measured on large crystals to smaller ones might lead to important mistakes and must therefore be avoided. Moreover, the influence of temperature must not be neglected: surface resistance may appear to be negligible at a given temperature (no effect of crystal size), but becomes predominant at a lower temperature. For a given separation, the presence of surface resistance must therefore be tested at the given separation temperature.

## 5 Conclusion

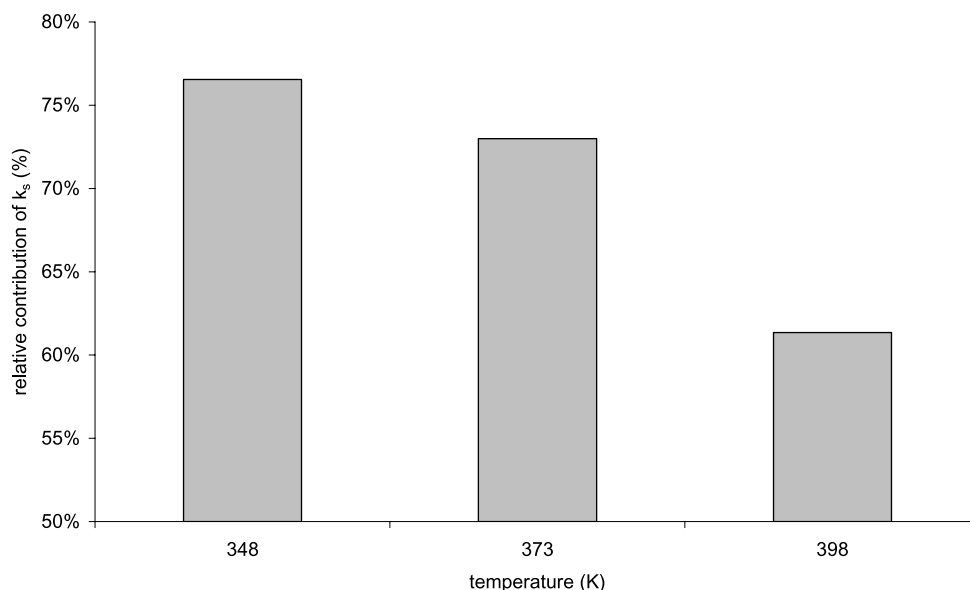
Uptake curves of cyclohexane were measured on crystals of Silicalite-1 with different sizes, for temperatures between

323 and 498 K. The crystals synthesis was optimised so as to obtain crystals with the same morphology. The resulting apparent diffusion coefficients vary with crystal size, showing the presence of a non negligible surface resistance. By applying a simple model, intracrystalline and surface resistances mass transfer coefficients were estimated.

Surface mass transfer coefficient was found to be in the same order of magnitude for the different samples and activated with temperature.

The surface of one of our sample was then purified by etching with a solution of hydrogen fluoride, without any enhancement of the adsorption kinetic. Surface resistance may not be located at the extreme surface of the crystals but in a layer of non negligible thickness of distorted crystal structure around the crystals.

**Fig. 12** Relative contribution of  $k_s$  as a function of temperature for 2  $\mu\text{m}$  crystals at 160 Pa



These results are very important, because they contribute to explain the well-known discrepancies between the diffusion coefficients experimental values.

In future work, these preliminary results will be validated by measurements on other molecules, such as branched alkanes (for which the literature diffusion coefficients are very dispersed).

Finally, dynamic molecular simulation of these systems should bring a very interesting insight about the origin of the surface resistance.

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