Determination of adsorption and diffusion parameters in zeolites through a structured approach

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Abstract

Temporal analysis of products (TAP) is a transient pulse-response technique that allows to extract kinetic information from reacting and adsorbing systems. In a previous work (Chem Eng Sci 57(2002) 1835), a detailed-transport model for the Multitrack set-up, a TAP-like system, was developed, which allows studying systems with a low bed resistance. The use of structured beds, having both a low bed resistance and small sorbent particles, is required to determine adsorption and diffusion parameters when strong adsorption and slow diffusion occurs. A method is presented to extend the range of measurable adsorption and diffusion parameters in zeolitic sorbents in the TAP technique by a structured approach. Small zeolite crystals are coated on larger non-porous glass beads. Adsorption and diffusion parameters for n-butane, SF_6 and 3-methylpentane have been determined in MFI-type zeolites. Absolute diffusivity values in the zeolite coating are estimated by using a well-defined silicalite sample as a reference to determine the effective diffusion length in the coating.

Two criteria have been derived, one for the characteristic time for transport through the bed, $0.05 \text{ s} < t_{bed} < 4 \text{ s}$, and one for the ratio of the latter and the characteristic diffusion time in the zeolite crystal, $0.01 < \alpha < 200 t_{bed}/(1 + t_{bed})$, which should be satisfied both to be able to determine values of the zeolite diffusivity.
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1. Introduction

Temporal analysis of products (TAP) is a transient pulse-response technique that allows to extract kinetic information from reacting and adsorbing systems (Gleaves et al., 1988). This experimental technique consists of a high-speed pulse valve, a packed bed micro-reactor under high vacuum, and a mass spectrometer. The experiments are carried out by pulsing a small amount of gas over a fixed bed of the sorbent or the catalyst located in a tubular reactor, and measuring the pulse response of the gas. By modeling these pulse responses, parameters like adsorption and diffusion parameters can be determined, as has been demonstrated for zeolites (Nijhuis et al., 1999a,b; Keipert and Baerns, 1998). Multitrack is an apparatus for performing transient measurements in ultra-high vacuum, which is based on this technique (Nijhuis et al., 1999a). A detailed model of the system has been developed recently (Delgado et al., 2002), using a new approach for modeling the pulse response, which allows studying systems with a low bed resistance. This new model provides a better reproduction of the initial part of the pulse, enabling to estimate the adsorption and diffusion parameters using small quantities of adsorbent, so that the time scale of the experimental pulses is reduced and the sensitivity of the technique is increased, because the signal-to-noise ratio is higher with lower bed resistance. The use of beds with a low resistance are becoming increasingly interesting (Shekhtman et al., 1999) especially when small particles have to be used due to strong adsorption and slow diffusion characteristics. The use of small particles, however, broadens the response signal appreciably, reducing the accurate determination of the kinetic parameters. This can be overcome by applying thin 'beds' of sorbents sandwiched between thicker layers of an inert material with larger particles, or by using 'structured packed beds'. Examples of these beds are those formed by glass beads or monoliths coated with small zeolite crystals, which simultaneously offer a large hydrodynamic 'bed' particle size, in

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combination with zeolite crystals having the proper characteristic diffusion time for the molecules under investigation. This structured catalyst approach allows the study of slowly diffusing molecules, and often relatively strongly adsorbing, in small-sized crystals without the drawback of large pulse broadening due to a packed bed with small particles. In this way the bed diffusion time and the intracrystalline diffusion time are decoupled and can be optimized independently. An important parameter in these systems is the effective diffusional length, which is not known a priori because it is very difficult to get a uniform zeolite coating accurately characterized.

The objectives of this work are (a) validation of the new model of the Multitrack system (Delgado et al., 2002) for adsorbing beds and demonstration of the structured approach through (b) estimation of the effective diffusion length in NaZSM-5-coated glass beads by comparing the diffusivities of n-butane and SF_6 in uniform silicalite-1 crystals and the coated beads, and finally (c) determination of the adsorption and diffusion parameters of 3-methylpentane (3-MP) on NaZSM-5-coated glass beads using this method.

2. Experimental

2.1. Materials

The silicalite-1 crystals with a ratio Si/Al > 1300 were synthesized in-house. The template inside the silicalite-1 crystals was removed by calcination at 873 K for 12 h. The apparent density of the sample was 1.76 g cm^{-3}, and the adsorption of N_2 indicated an accessible microporous void volume of 0.179 cm^3 g^{-1} and a microporous area of 372 m^2 g^{-1}. The silicalite-1 crystals had a uniform shape and size of about $120 \times 50 \times 50$ μm ($L \times H \times W$), as determined by SEM (Zhu et al., 2001b). SF_6 and n- butane were obtained from Hoekloos with a specified purity over 99% and were used without further purification. Argon (for the estimation of the bed tortuosity in the Multitrack reactor) was obtained from Hoekloos (99.9999%). 3-MP was obtained from Aldrich ($> 99\%$) and was used without further purification. Sodium aluminate (Merck) and tetraethylorthosilicate (Merck) were used as sources for aluminum and silicon in the NaZSM-5-coating.

2.2. Preparation of NaZSM-5-coated glass beads

The detailed method for preparing the NaZSM-5-coated glass beads is described elsewhere (Van der Linde, 1999). Briefly, glass beads with an average diameter of 650 μm were cleaned with 20% HNO$_3$ for 1 h and calcined at 825 K for 24 h to avoid fragmentation during or after synthesis. The glass beads were immersed in the zeolite synthesis solution in a rotating autoclave and the system was allowed to crystallize for 16 h at 443 K, the autoclave being rotated every 30 min. After the synthesis, the solution was removed and
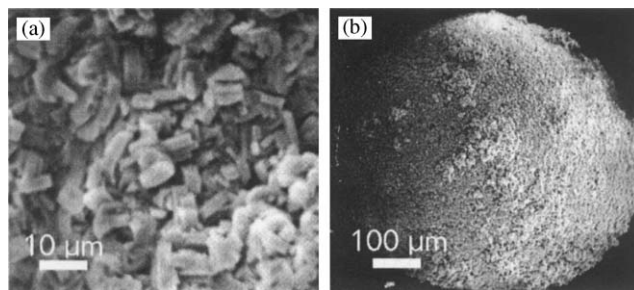

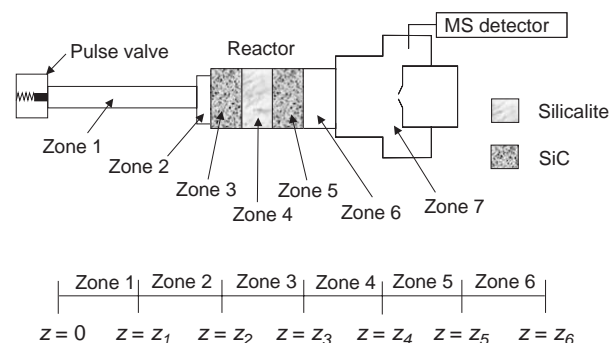Fig. 1. SEM photographs of a NaZSM-5-coated glass bead.

Fig. 2. Scheme of the Multitrack set-up (Reactor 2), indicating the different zones considered in the model of the system.

the beads were washed with distilled water, dried and calcined at 825 K for 32 h to remove template molecules. The ZSM-5-coated beads had a Si/Al ratio of 19, and were analyzed by X-ray diffraction (XRD), nitrogen adsorption and scanning electron microscopy (SEM). A SEM photograph of a coated bead is shown in Fig. 1. The XRD profile confirmed the crystalline phase of ZSM-5. The amount of ZSM-5 present on the beads was determined by nitrogen adsorption, which resulted in an adsorption of 0.1 mmol of nitrogen per gram of coated beads. Since the amount of adsorbed nitrogen by pure ZSM-5 is known (3.59 mmol N_2/g ZSM-5), the amount of ZSM-5 coating on the beads can easily be deduced. An average thickness of 21 μm of the assumed uniform ZSM-5 layer was derived from the estimated volume of the zeolite coating (amount of ZSM-5 g/1.8 g cm^{-3} zeolite) divided by the external geometric bead surface area.

2.3. Adsorption and diffusion studies with the Multitrack

The adsorption–diffusion experiments in silicalite-1 and the coated beads were carried out in the Multitrack system. A detailed description of the experimental set-up can be found elsewhere (Nijhuis et al., 1999a,b; Delgado et al., 2002). Two different reactor configurations (Reactor 1 and Reactor 2) were used in this work, following the same notation as in a previous work (Delgado et al., 2002). A scheme of Reactor 2 charged with a sorbent bed is shown in Fig. 2, indicating the different zones used in the numerical

resolution of the model. Zone 7 represents the vacuum chamber. Reactor 1 was charged with coated beads only, resulting in a bed of 6 mm, and Reactor 2 with a composite packing of three consecutive beds (3.6 mm of silicon carbide, 3.3 mm of silicalite-1, and 3.6 mm of silicon carbide). For Reactor 1, it was assumed that the bed porosity was 0.4 for spherical particles. For Reactor 2, it was assumed that the porosity and tortuosity of the inert and adsorbing beds were the same for modeling purposes, the estimated average porosity being 0.55. The radius of the beads including the coating was 346 μm, the average size of the SiC particles was 230 μm, and the equivalent radius of the silicalite-1 particles (assuming cylindrical geometry) was 20.7 μm.

3. Model description

The modeling of the mass transfer in the void and inert zones in the Multitrack system is explained in detail elsewhere (Delgado et al., 2002). Here, only the modeling of the adsorbing bed dynamics will be described. It is assumed that the gas in the voids is in equilibrium with the adsorbent surface. The mass balance inside the particles is given by

$$\frac{\partial q}{\partial t} = \frac{D_{\text{pore}}}{r_p^2}\left(\frac{s}{x}\frac{\partial q}{\partial x} + \frac{\partial^2 q}{\partial x^2}\right),$$ (1)

where D_{pore} is the intracrystalline diffusivity. The parameter s takes into account the adsorbent geometry, being 1 for the silicalite crystals (cylindrical) and 2 for the coated beads (spherical). The boundary conditions for this equation are

$$x = 0 \qquad \frac{\partial q}{\partial x} = 0 \text{ (silicalite crystals)},$$

$$x = \frac{346 - 21}{346} \quad \frac{\partial q}{\partial x} = 0 \text{ (coated beads)}, \quad (2)$$

$$x = 1 \quad q = K_H p, \quad (3)$$

where 346 μm is the total bead radius and 21 μm is the coating thickness. This boundary condition indicates that the flux is zero at the glass bead surface. K_H is the Henry's law constant, indicative of the gas-surface affinity. It is assumed that the transport in the interparticle voids occurs by Knudsen diffusion. The assumption of Knudsen diffusion for the least favorable case, i.e. the pulse with a non-adsorbing gas has been verified previously (Delgado et al., 2002). The mass balance for the bed void space is given by

$$\frac{\partial p}{\partial t} = \frac{D_K}{\tau}\frac{\partial^2 p}{\partial z^2} - \frac{s+1}{r_p^2}\frac{(1-\varepsilon)}{\varepsilon}D_{\text{pore}}\rho_p RT \left.\frac{\partial q}{\partial x}\right|_{x=1}, \quad (4)$$

with the boundary conditions

$$z = z_{\text{initial}} \quad p = \text{pressure at } z \text{ initial in the previous zone},$$ (5)

$$z = z_{\text{final}} \quad D_K\frac{\partial p}{\partial z} = \text{flux at } z \text{ final in the following zone}.$$ (6)

The Knudsen diffusivity in the voids is calculated from the average interparticle distance with the following expression:

$$D_K = \frac{2}{3}\left(\frac{2\varepsilon r_p}{3(1-\varepsilon)}\right)\sqrt{\frac{8RT}{\pi M}}. \quad (7)$$

The tortuosity of the beds is estimated experimentally, as it is discussed later. The initial condition for the interparticle voids is $p = 0$, like for the rest of zones. Although there is some background pressure in the system (10^{-4} Pa), it is not relevant in the modeling.

The new normalized signal proposed in a previous work (Delgado et al., 2002), which can be compared with the experimental normalized signal for the estimation of model parameters, is given by

$$N.S. = Q_{\text{pump}}\frac{p_{VC}}{RT_{VC}}\frac{N_A}{N_{\text{mol}}} \quad (8)$$

where N_{mol} is the pulse size (10^{14} molecules). This equation expresses that the number of molecules injected must be equal to the number of molecules removed by the vacuum pumps. The vacuum chamber is always at room temperature ($T_{VC} = 298$ K). It is important to note that the number of different zones considered in the complete model (Fig. 2), together with the use of this normalized signal, complicates enormously the resolution with an analytical method, since the mass balance in the vacuum chamber must be taken into account in the boundary condition at the outlet of the reactor.

4. Numerical methods

The model is solved numerically using the PDECOL package (Madsen and Sincovec, 1979), which uses orthogonal collocation on finite elements (OCFE) technique for the discretization of one spatial variable. The application of the method to the PDE resulting from the mass balance in the axial coordinate has been described elsewhere (Delgado et al., 2002). Hermite polynomials of third degree were used for the radial (particle) coordinate discretization (Finlayson, 1980). Four increments in the axial coordinate (in each zone, for both reactor configurations used in this work) and four increments in the radial coordinate were enough to observe no change in the modeled pulse response when the number of increments was increased. The optimal parameter values in the fitting of experimental pulse responses were obtained by minimizing the sum of squared residuals of the normalized MS-signal (Delgado et al., 2002).

5. Results and discussion

5.1. Estimation of the bed tortuosities

In order to estimate the bed tortuosity of the studied reactors experimentally, which is the only unknown parameter to fully describe the dynamics of the whole Multitrack system, the model was fitted to argon pulses for Reactors 1 and
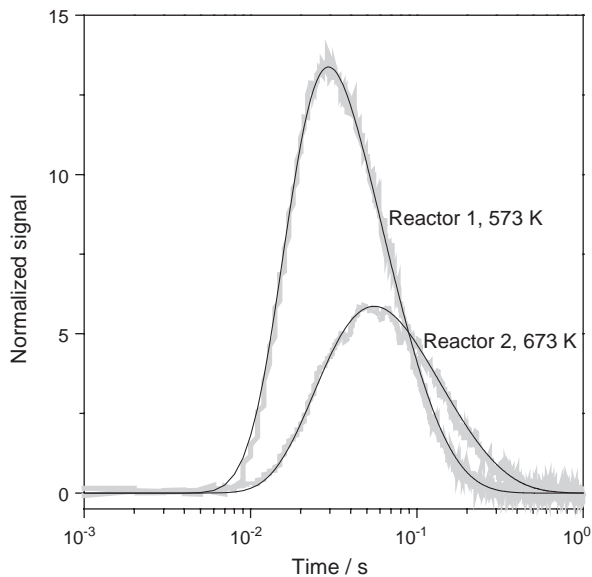
Fig. 3. Experimental (gray lines) and modeled pulse responses (solid lines) for argon through Reactors 1 (coated beads) and 2 (silicalite-1 and SiC).

Fig. 4. Arrhenius plot of the estimated Henry's law adsorption constants for the studied systems.; (▲) SF_6 in NaZSM-5 beads; (△) SF_6 in silicalite crystals; (●) n-butane in NaZSM-5 beads; (○) n-butane in silicalite crystals; (■) 3-MP in NaZSM-5 beads; (□) fixed values for diffusivity estimation for 3-MP; (solid line) calculated Arrhenius line.

Fig. 5. Arrhenius plot of the estimated diffusivities for the studied systems. For the definition of f, see Eqs. (14) and (15). (●) n-butane; (▲) SF_6; (■) 3-MP (corrected with f); (□) estimated with fixed K_{ads}; (solid line) NaZSM-5 beads; (dashed line) silicalite crystals.

2 with a bed temperature high enough to consider argon as an inert, non-adsorbing gas for MFI zeolites (Dunne et al., 1996a,b). A good reproduction of inert pulses is required for the determination of adsorption–diffusion parameters. The comparison between the experimental and calculated pulse responses is shown in Fig. 3, where a good reproduction is observed. The broader pulse for the bed of silicalite crystals is due to the larger resistance caused by the smaller particle size and the longer total bed. The estimated tortuosities for the coated beads and silicalite crystals were 1.29 and 3.35, respectively. Once the transport parameters of both systems were determined, they were fixed for the estimation of the Henry's law constant and the intracrystalline diffusivity of the studied gases in silicalite-1 and NaZSM-5, which are the only adjustable parameters in the model.

5.2. Estimation of the diffusion length in the NaZSM-5-coated beads and determination of the adsorption diffusion parameters of 3-MP in the coated beads

A set of experiments with the Multitrack system were performed to obtain the pulse responses of n-butane and SF_6 with the NaZSM-5-coated beads and the silicalite crystals at several bed temperatures, which were fitted with the proposed model, with the objective of validating the model for adsorbing beds, and for estimating the effective diffusional length in the coated beads by comparison of the diffusivities in the silicalite crystals and the coated beads. Another set of experiments were performed with 3-MP and the coated beads to estimate the adsorption and diffusion parameters of this sorbate in this system. The estimated values
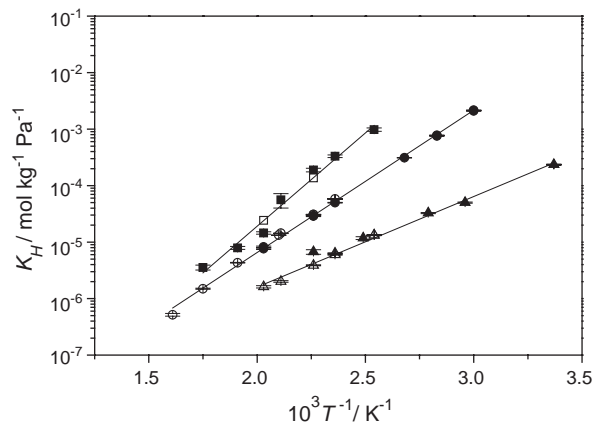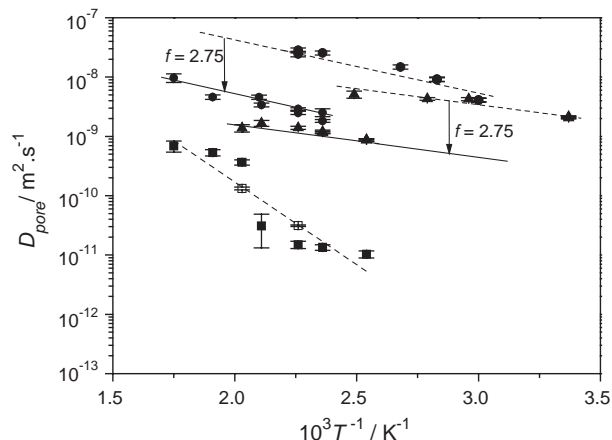
of the Henry's law constant and the diffusivity are shown in Figs. 4 and 5, respectively. A comparison between the experimental and the calculated pulse responses is shown in Fig. 6. It is observed that the proposed model reproduces the experimental pulses of adsorbing gases excellently for both bed configurations. The estimated values of the Henry's law constant and the adsorption heats are virtually the same for both sorbents, so they behave in this respect fairly similar, although literature indicates slightly increased heats of adsorption due to the presence of Na-ions (Dunne et al., 1996b). The further good agreement with literature (Table 1 and Table 2, which is discussed later) confirms the validity of the model for adsorbing systems, including the coated beads. The diffusivities of n-butane and SF_6 were significantly higher for the NaZSM-5-coated beads than for
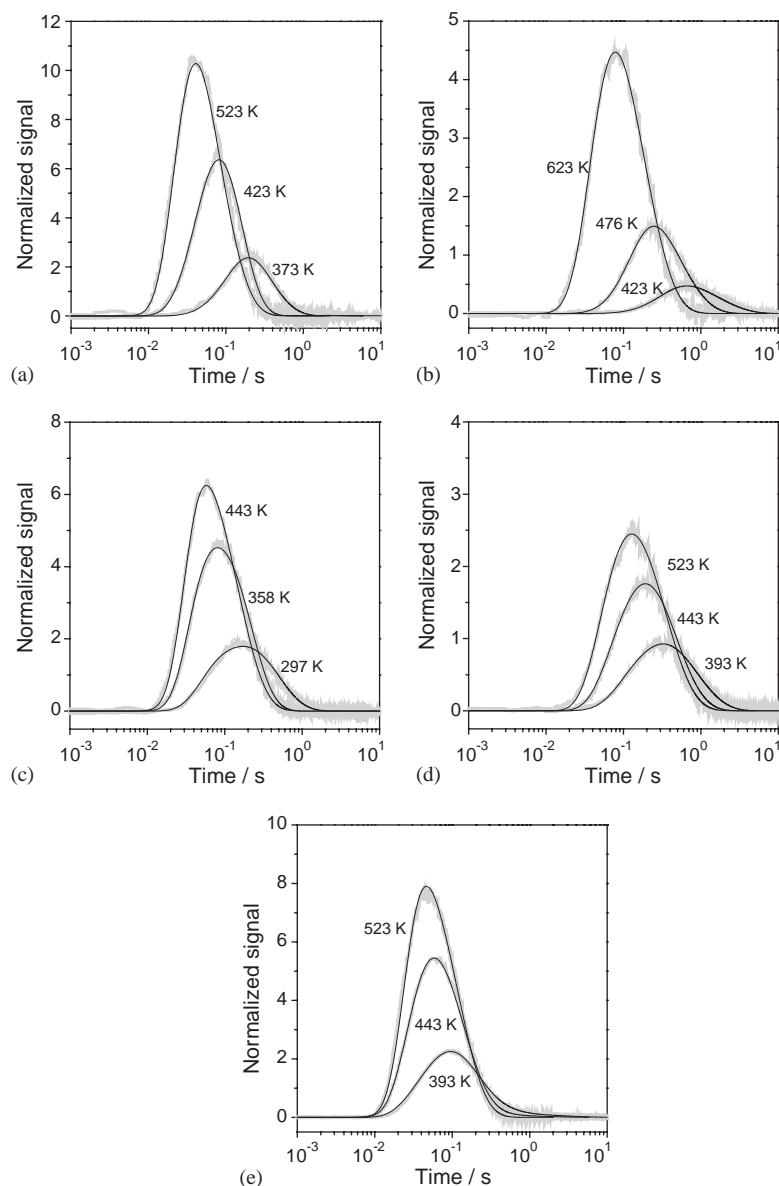
Fig. 6. Experimental (gray lines) and modeled pulse responses (solid lines) for the studied systems. (a) *n*-Butane on NaZSM-5-coated beads, (b) *n*-Butane on silicalite-1 crystals. (c) SF_6 on NaZSM-5-coated beads. (d) SF_6 on silicalite-1 crystals. (e) 3-MP on NaZSM-5-coated beads.

silicalite, despite that both sorbents have the same pore structure, indicating that the assumed diffusional length for the beads' coating as a uniform smooth layer is erroneous, as it can be expected from the non-uniform granular structure of the coating (Fig. 1). Therefore, a diffusional length shorter than the assumed one may be anticipated. In this respect, it is important to note that the estimated diffusivities follow a similar Arrhenius dependence in both systems, and that they correlate well with the molecular diameter of the sorbate, this parameter being larger for SF_6 (Webster et al., 1998). Moreover, a lower diffusivity with a higher activation energy of diffusion is obtained with 3-MP, which is explained in terms of the similarity between its kinetic diameter and the pore size of MFI zeolites ($\sim 5.1 \times 5.5$ Å), resulting in a

strong steric hindrance in the diffusion process (Cavalcante and Ruthven, 1995a). The estimated Henry's constants and diffusivities for 3-MP in the coated beads had a larger error than the ones estimated for the other systems, which was attributed to a significant correlation between the Henry's constant and the diffusivity in the fitting procedure for this sorbate. For the experiments with the largest error, the value of the Henry's constant was fixed to the expected value according to the observed Arrhenius dependence of this parameter (Fig. 4), resulting in diffusivities which also fall into the expected Arrhenius line for the diffusivity (Fig. 5), confirming the correlation between them.

It is important to remark that the adsorption and diffusion parameters of 3-MP in NaZSM-5 could only be estimated

Table 1
Comparison of the estimated Henry's law constants at 300 K and heats of adsorption with literature values

Gas	Sorbent	K_H at 300 K mol kg^{-1} Pa^{-1}	ΔH_{ads} kJ mol^{-1}	Technique[a]	Reference
n-Butane	Silicalite-1	0.024	51	MT	This work
	Silicalite-1	0.010	43	MT	Nijhuis et al. (1999a)
	Silicalite-1	0.037	49–56	TEOM	Zhu et al. (2000)
	Silicalite-1	0.06	50	CPC	Hufton and Danner (1993)
SF$_6$	Silicalite-1	2.0×10^{-4}	31	MT	This work
	Silicalite-1	2.8×10^{-4}	33	ZLC	MacDougall et al. (1999)
	Silicalite-1	3×10^{-4}	34	CVM	Dunne et al. (1996a)
	NaZSM-5		38–40		Dunne et al. (1996a)
	HZSM-5		35		
	Silicalite-1		35	TG	Sun et al. (1998)
3-MP	NaZSM-5	0.70	63	MT	This work
	Silicalite-1	0.64	60–66	TEOM	Zhu et al. (2001a)

[a]MT=Multitrack, TEOM = tapered element oscillating microbalance, ZLC= zero length column, CVM=calorimetric-volumetric method, TG =thermo-gravimetry.

Table 2
Comparison of the estimated diffusivities at 423 K and activation energies of diffusion with literature values

Gas	Sorbent	D_{pore} at 423 K (m^2 s^{-1})	E_{diff} (kJ mol^{-1})	Technique[a]	Reference
n-Butane	Silicalite-1 and NaZSM-5	2×10^{-9}	18	MT	This work
	Silicalite-1	1.1×10^{-9}	7.3	MT	Nijhuis et al. (1999a)
	Silicalite-1	5×10^{-9}	8	PFGNMR	Heink et al. (1992)
	Silicalite-1	4×10^{-10}	21	FR	Van den Begin et al. (1989)
SF$_6$	Silicalite-1 and NaZSM-5	1×10^{-9}	10	MT	This work
	Silicalite-1	3×10^{-11}	19	ZLC	MacDougall et al. (1999)
3-MP	NaZSM-5	2×10^{-11}	53	MT	This work
	Silicalite-1	8×10^{-13}	52	TEOM	Zhu et al. (2001b)
	Silicalite-1	2×10^{-12}	57	Gravimetric	Cavalcante and Ruthven (1995b)

[a]MT=Multitrack, PFG-NMR=pulsed field gradient-NMR, TEOM=tapered element oscillating microbalance, ZLC= zero length column, FR=frequency response.

using a bed of the zeolite-coated glass beads with a relatively large bed diameter (Reactor 1, 12 mm), due to the strong adsorption and slow diffusion properties of 3-MP in this sorbent. This already demonstrates that this configuration allows extending the region of measurable diffusivities. This point is illustrated further in Fig. 7, where the theoretical pulse responses for 3-MP in NaZSM-5 are shown for several sorbent-reactor configurations, in order to see if the adsorption and diffusion parameters can be estimated from the pulse response obtained in each case. The estimated values of the Henry's law constant and the diffusivity were used in the simulations. A valid pulse response must have a height at its maximum not lower than about a 5% of the height of an inert pulse response (no adsorption), of course depending on the instruments' detection sensitivity. For this reason, the inert pulse response is also included in the graphs for comparison's sake. The pulse signal must also

return to the baseline before ~ 15 s, in order to get a reliable integration of the pulse response. This integration is necessary to normalize the experimental signal and to compare it with the calculated one. In all cases, the same amount of zeolite and the same temperature are considered, 0.125 g and 393 K, the amount of zeolite being equal to the one used in the experiments with the coated beads. Fig. 7(a) show the pulse response for large zeolite particles (346 μm of radius) in Reactor 2, Fig. 7(b) for small zeolite particles (20.7 μm) packed between inert beds in Reactor 2, and Fig. 7(c) for the zeolite coated beads in Reactors 1 and 2.

At first sight, the results in Fig. 7(a) seem to indicate that using large particles leads to valid pulse responses. However, the enlarged graph shows that a long tail is obtained in this case, which makes it difficult to integrate the signal adequately. The area below the curve from 0 to 1 s, when the signal seems to have reached the baseline, is only the 90% of
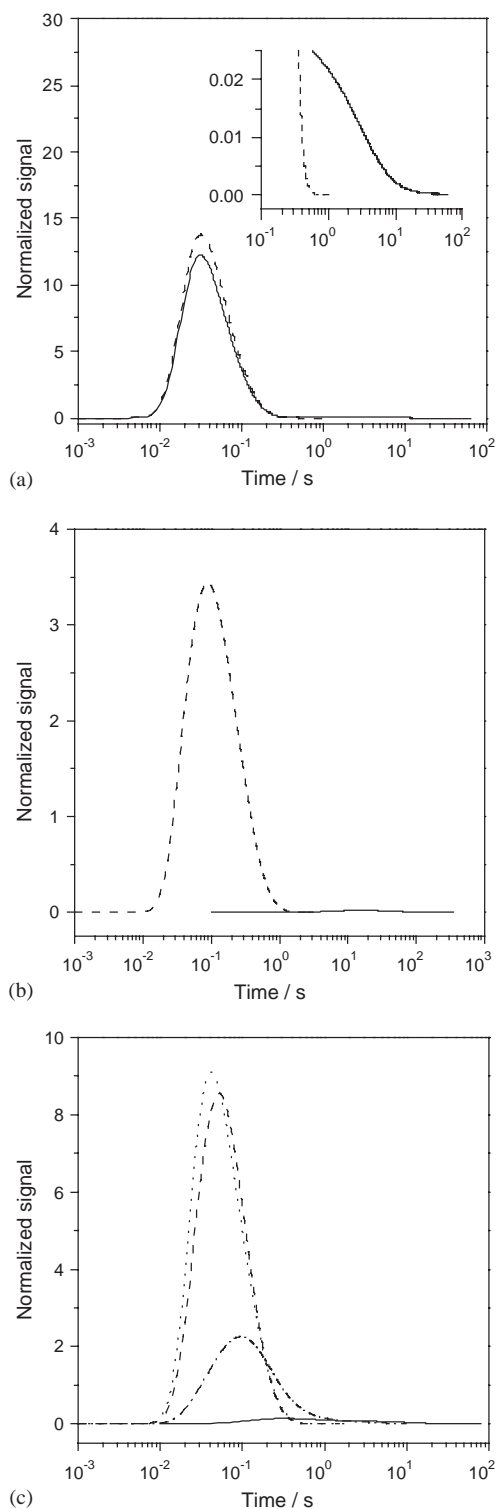
(a)

(b)

(c)

Fig. 7. Theoretical pulse responses (continuous lines) for 3-MP in NaZSM-5 at 393 K for several sorbent-reactor configurations. The dashed lines correspond to an inert pulse. (a) Large zeolite particles (346 μm of radius) in Reactor 2. (b) Small zeolite particles (20.7 μm) packed between inert beds in Reactor 2. (c) Coated beads in Reactors 1 and 2. In this graph, the continuous and the dashed lines correspond to Reactor 2 (7 mm⌀), and the dash-dot and dotted lines to Reactor 1 (12 mm ⌀) for 3-MP and inert gas, respectively.

the total area. Furthermore, it is generally not straightforward to synthesize these large uniform crystals for all zeolites.

Fig. 7(b) shows that the use of small particles results in very broad pulse responses, not suitable for estimation purposes.

The results in Fig. 7(c) show that a poor pulse response is obtained with coated beads in Reactor 2 (7 mm of diameter). However, a good response is obtained with Reactor 1 (12 mm of diameter), due to the shorter length of the bed in this case (6 mm instead of 17.6 mm). The shorter length results in a lower bed resistance, proportional to the square of the bed length. Reactor 1 charged with the same amount of large or small zeolite particles would result in a very short bed (1 mm), very difficult to realize in practice. Therefore, the use of coated beads in a relatively short bed allows to extend the range of diffusion parameters measurable with the Multitrack (TAP) technique. In order to find a quantitative criterion to determine when, for a given Henry's law adsorption constant and zeolite diffusivity, a bed configuration leads to a valid pulse response, the effect of the bed configuration and the adsorption and diffusion parameters on the sensitivity was simulated with the model of the system. It was concluded that the validity of the pulse depended on two parameters, the maximum bed diffusion time (t_{bed}), which takes into account the total bed resistance, including the retarding effect of adsorption, and the ratio of the maximum bed diffusion time to the particle diffusion time ($\alpha = t_{bed}/t_{particle}$). These parameters are defined as follows:

$$t_{bed} = \frac{L_{bed}^2}{\left(\dfrac{D_{Kbed}\varepsilon}{\tau}\right)}[\varepsilon + (1-\varepsilon)(1-c^3)K_{dH}], \qquad (9)$$

$$t_{bed} = \frac{\ell^2}{D_{pore}}, \qquad (10)$$

$$\alpha = \frac{t_{bed}}{t_{particle}}. \qquad (11)$$

The maximum bed diffusion time was defined on the basis of a previous study (Delgado et al., 2002), and represents the bed diffusion time if no internal resistance was present. The parameter c is included to account for the volume fraction of zeolite in the use of a coated spherical sorbent, and represents the ratio of the radial position where the coating starts to the total particle radius. K_{dH} is the dimensionless Henry's constant ($m_{void}^3/m_{sorbent}^3$), and ℓ is the particle diffusion length. For systems with a packing between inert beds, the corresponding diffusion times can be added to the diffusion time estimated with Eq. (9), although they are negligible when adsorption is important. The following criteria were used to consider a pulse response as valid, which should be fulfilled simultaneously: (i) difference between the height at the pulse maximum and that of an inert pulse > 5% OR the difference between the respective times of the maxima > 5%; (ii) difference between the height of the pulse maximum and that of a pulse with infinite diffusivity, with the same bed diffusion time, > 2% OR the difference between

Table 3
Comparison of characteristic diffusion times in the simulation of Fig. 7 at 393 K

Configuration	Reactor	t_{bed} (s)	$t_{particle}$ (s)	α
Fig. 7(a)	R2	3	1300	0.0023
Fig. 7(b)	R2	71	4.6	15
Fig. 7(c)	R1	2.1	4.8	0.44
	R2	18	4.8	3.8

the respective times $> 2\%$; (iii) area below the pulse up to 10 s > 0.95.

By fixing t_{bed} to values ranging from 0.01 to 10 s, and changing $t_{particle}$ between 0 and infinite, it was determined that valid pulse responses are obtained when 0.05 s $< t_{bed} < 4$ s, and $0.01 < \alpha < 200 t_{bed}/(1+t_{bed})$. Both conditions must be satisfied, and are valid for both Reactors 1 and 2. It must be noted that these criteria are not based on dimensionless numbers obtained from the model equations, but only on the empirical study of the influence of the bed and particle diffusion times. The complexity of the model, which cannot be solved analytically, makes it very difficult to obtain rigorously the parameters that determine the sensitivity of the pulse signal to the adsorption and diffusion parameters. For $t_{bed} > 4$ s, the tailing of the pulses is too long to be integrated properly, and/or the pulse height is too low, and for $t_{bed} < 0.05$ s, the difference between an inert pulse and one with infinite diffusivity is too small. The maximum measurable particle diffusion time is proportional to the bed diffusion time because the bed adsorption capacity increases with the latter. The minimum measurable particle diffusion time also increases with the maximum bed diffusion time, because the retarding effect of diffusion is less visible the larger the bed diffusion time. The upper limit of α therefore varies between 10 and 160, depending on the bed diffusion time. For low bed times, the upper limit of α indicates that the minimum particle diffusion time does not depend on the bed diffusion time, because the main resistance to the axial transport is located in zone 1 of the reactor (Fig. 2). These criteria are more general than the ranges of measurable diffusivities indicated in the papers of Keipert and Baerns (1998) and Nijhuis et al. (1999b).

Table 3 shows the results of applying the proposed criterion to the simulations performed in Fig. 7. It is observed that Reactor 1 with coated beads (Fig. 7(c)) is the only configuration resulting in valid pulse responses, because Reactor 2 with large particles (Fig. 7(a)) has a quite large particle diffusion time, with $\alpha < 0.01$, Reactor 2 with small particles (Fig. 7(b)) has a very large bed diffusion time, larger than 4 s, and Reactor 2 with coated beads (Fig. 7(c)) has a lower bed diffusion time, but still larger than 4 s. This exemplifies the effect of decoupling the time scales by a structured approach. The use of the coating is especially effective to reduce the bed diffusion time with respect to the configuration with small particles, with practically the same particle diffusion time.
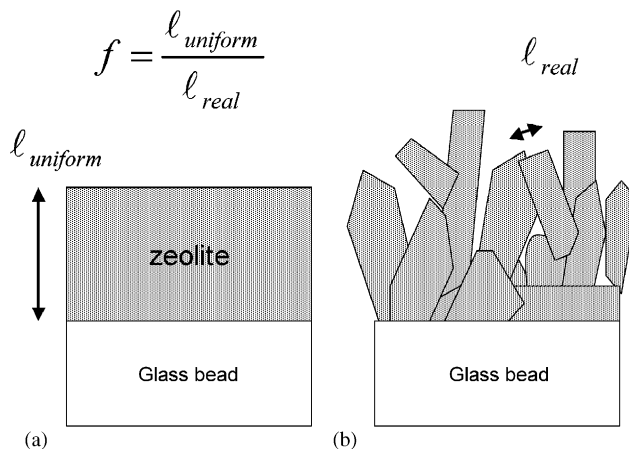

Fig. 8. Schematic representation of the idealized uniform zeolite coating and the rough coating of intergrown crystals, and their diffusion lengths.

In order to estimate the diffusional length in the NaZSM-5- coated beads, it was assumed that the diffusivity of n-butane and SF_6 is the same for both systems. Consequently, differences in absolute value of the diffusivity, calculated from the estimated diffusivity time $t_{particle}$, are attributed to a wrong value of the diffusion length ℓ for the coated beads. Hence, the diffusivities were corrected by a constant factor f, for both components. Taking the silicalite-1 as a reference, the diffusivities of these gases in silicalite may be expressed as

$$(D_{n\text{-butane}})_{silicalite} = D_{0 n\text{-butane}} \exp\left(\frac{-E_{\text{diff } n\text{-butane}}}{RT}\right), \quad (12)$$

$$(D_{SF6})_{silicalite} = D_{0\ SF6} \exp\left(\frac{-E_{\text{diff SF6}}}{RT}\right) \quad (13)$$

and in the NaZSM-5-coated bead as

$$(D_{n\text{-butane}})_{NaZSM-5} = f^2 D_{0\ n\text{-butane}} \exp\left(\frac{-E_{\text{diff } n\text{-butane}}}{RT}\right) \quad (14)$$

$$(D_{SF6})_{NaZSM-5} = f^2 D_{0\ SF6} \exp\left(\frac{-E_{\text{diff SF6}}}{RT}\right), \quad (15)$$

where f is the correction factor, equal to the assumed diffusional length, the average coating thickness of 21 μm, divided by the real effective one. This model was fitted to all the diffusivity data for both gases leaving as adjustable parameters $D_{0\ n\text{-butane}}$, $D_{0\ SF6}$, $E_{\text{diff } n\text{-butane}}$, $E_{\text{diff SF6}}$ and f, resulting in the following optimal parameter values: $D_{0\ n\text{-butane}} = 3.5 \times 10^{-7}$ m^2 s^{-1}, $D_{0\ SF6} = 1.9 \times 10^{-8}$ m^2 s^{-1}, $E_{\text{diff } n\text{-butane}} = 17.5$ kJ mol^{-1}, $E_{\text{diff SF6}} = 10.3$ kJ mol^{-1}, $f = 2.75$. This result implies that the effective diffusion length for the zeolite coating is 8 μm. In view of Fig. 1 this is not a surprise, the coating is not a smooth uniform layer, but consists of many intergrown crystals resulting in a rough surface, schematically depicted in Fig. 8. Due to this roughness, the averaged diffusion length is shortened.

A comparison between the experimental and the calculated diffusivities is shown in Fig. 5 (solid and dashed lines). It is observed that the proposed model reproduces the diffusivity data well, using the same correction factor for n-butane and SF_6, which shows that this approach can be used to determine the effective diffusional length in structured sorbents. Once this diffusional length in the coated beads was known, the real diffusion parameters for 3-MP in this sorbent were estimated, showing the big difference between the diffusivities of 3-MP and the other sorbates (Fig. 5). The estimated diffusivities and the activation energies are compared with literature values obtained with other techniques in Table 2. It is observed that, except for the NMR values, the diffusivities in the Multitrack system are significantly higher than the ones estimated with other techniques, but the activation energies of diffusion are of the same order of magnitude. The better agreement between TAP results and NMR data has been observed earlier (Nijhuis et al., 1999a,b). The higher diffusivity in the Multitrack could be attributed to the absence of inert carrier gas in this technique, which may lead to a higher mobility of the sorbate inside the zeolitic pores. Indeed, a significant reduction in the intracrystalline diffusivity of alkanes due to the presence of inert gases inside the pore network (by a factor of six times or more) has recently been demonstrated experimentally for several zeolites (Mittelmeijer-Hazeleger et al., 2002), including the MFI ones, although this does not apply to all techniques.

It must be noted that the activation energy of diffusion in this work for n-butane is higher than the value obtained in a previous study (Table 1). The major difference between these studies being the use of twinned crystals by Nijhuis et al. (1999a). Preliminary experiments indeed indicate differences between twinned and untwinned crystals, but further work is needed to yield more insight on this point. For 3-MP, the activation energies of diffusion estimated with different techniques are very similar, indicating that the energy barrier for diffusion is fairly similar in all cases, so the presence of differences, if any, should be subtle. For other alkanes in silicalite, differences between the activation energies of diffusion obtained with different techniques are not rare (Maginn et al., 1996). The higher pre-exponential constant for the diffusivity of 3-MP in the Multitrack system may indicate the uncertainty in the estimation of the diffusion length in all studies. Presence of cracks, crystal twinning, etc. all may lead to overestimation of this parameter, and comparison of absolute values should be applied with caution, whereas the temperature dependency is a better indicator.

In the determination of the effective diffusion length, it has implicitly been assumed that the sorption and diffusion properties of the silicalite-1 and the Na-ZSM-5-coated beads are similar. The results presented here strongly indicate this, considering the temperature dependencies of the diffusivities and the similar adsorption values (Kärger and Ruthven, 1992). It could be questioned whether especially the diffu-

sion would not differ strongly, due to the presence of Na ions coordinated near the framework aluminum in the structure. The unit cell of the MFI structure contains 96 SiO_2 units, with four straight and four zig-zag channel sections and four channel intersections where molecules can adsorb (Trout et al., 1997). For a Si/Al ratio of 19 in this Na-ZSM-5 sample, about five Na ions are present per 12 sorption locations, so around 40%. According to percolation theory (Trout et al., 1997), if Na would block these locations there should be a drastic drop in the diffusivity in NaZSM-5 compared to silicalite, as the percolation transition occurs, at the 36% of blocked sites. If some blocking occurs, this does in principle not affect the diffusivity itself nor the temperature dependency, but may lead to an apparent longer diffusion length, i.e. affect the value of f.

In practice full blocking does not occur, since generally the cations can be completely exchanged by other, but hindrance may be present, but this depends on the location in the structure. Most studies with respect to the distribution of the Al is related to its 'pair' formation, since many cations used in ion exchange procedures to introduce catalytic properties in zeolites are divalent (Rice et al., 1999; Dedecek et al., 2002; Trombetta et al., 2000). Theoretical simulations assume random or Poisson distributions of Al in the framework (Rice et al., 1999), but experimental work does not support this and indicate that it strongly depend on the synthesis method (Dedecek et al., 2002). A large fraction (up to 75%) of the Al-pairs are located near the intersections of the straight and zig-zag channels. This would result in a minimal hindrance towards diffusion. Support for this is found in permeation studies through ZSM-5 membranes exchanged with cations of different size (Aoki et al., 2000). For a Si/Al ratio of 25, the flux difference between H- and Na-ZSM-5 membranes is absent for molecules as SF_6, and n- and i-butane. Larger cations reduced the permeation flux, indicating increased hindrance. The permeation selectivity for normal and iso-butane mixtures, however, did not change for these different cations, which led these authors to suggest that the location of the cations is mostly in the vicinity of the channel intersections where the effect on the permeating molecules is minimal. The current results seem to support a similar conclusion.

6. Conclusions

Adsorption and diffusion parameters in zeolite crystals can be well determined by the high vacuum TAP pulse technique, as has been well documented (Keipert and Baerns, 1998; Nijhuis et al., 1999a,b). A method has been presented to extend the window of measurable adsorption and diffusion parameters in zeolitic sorbents in the TAP technique by a structured approach. Small zeolite crystals are coated on larger non-porous glass beads. In this way the diffusion times of the transport through a packed bed and diffusion in the zeolite crystal are decoupled and can be chosen more

independently, and allows the study of small crystals. Adsorption parameters and diffusion activation energies for *n*-butane, SF_6 and 3-MP correspond well with literature, demonstrating the approach. For calculating absolute values of the diffusivity the proper value of the zeolite diffusion length is essential. This calibration can be achieved by using a well-defined sample in a packed bed configuration as a reference.

In order to be able to determine values of the zeolite diffusivity two criteria should be satisfied simultaneously, one for the characteristic time for transport through the bed, $0.05\text{ s} < t_{\text{bed}} < 4\text{ s}$, and one for the ratio of the latter and the characteristic diffusion time in the zeolite crystal, $0.01 < \alpha < 200 t_{\text{bed}}/(1 + t_{\text{bed}})$.

Notation

c	parameter defined in Eq. (9)
D	diffusivity, $m^2\ s^{-1}$
E	activation energy, $kJ\ mol^{-1}$
f	(assumed diffusional length)/(real diffusional length)
K_H	Henry's law constant, $mol\ kg^{-1}\ Pa^{-1}$
K_{dH}	dimensionless Henry's law constant
ℓ	particle diffusion length, m
L_{bed}	bed length, m
M	molecular weight $kg\ mol^{-1}$
N_A	Avogadro's number, molecules mol^{-1}
N_{mol}	number of molecules in a pulse
p	pressure, Pa
q	adsorbed concentration, $mol\ kg^{-1}$
Q_{pump}	pumping rate, $m^3\ s^{-1}$
R	gas constant, $J\ mol^{-1}\ K^{-1}$
r	radius, m
s	parameter defined in Eq. (1)
T	temperature, K
t	time, s
x	dimensionless radial coordinate
z	axial coordinate, m

Greek letters

α	parameter defined in Eq. (11)
ε	bed porosity
ρ	density $kg\ m^{-3}$
τ	bed tortuosity

Subscripts

0	pre-exponential constant
diff	diffusion
K	Knudsen
p	particle
pore	zeolitic pore
VC	vacuum chamber

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