Adsorption (2010) 16: 29–36
DOI 10.1007/s10450-010-9205-6

PROCEEDINGS OF PBAST5

Diffusion of linear paraffins in silicalite studied by the ZLC method in the presence of CO_2

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Received: 1 August 2009 / Accepted: 25 January 2010 / Published online: 11 March 2010

Abstract The diffusion behavior of C_4–C_{10} *n*-alkanes in silicalite-1 has been investigated by using the Zero Length Column method. The diffusivities derived from measurements at different purge rates with different purge gases confirming intracrystalline diffusion control. Data are compared with results reported in the literature for MFI zeolites. The diffusivities were found to be consistent and agree well with data previous obtained by ZLC. However, these data showed a remarkable disagreement with other reported techniques (PFG-NMR, QENS and Permeation). The eventual influence of carbon dioxide (CO_2) adsorption on diffusion properties of *n*-alkanes in silicalite was also investigated. For this purpose, a series of experiments was performed involving hydrocarbons mixed with CO_2. Data were obtained at 303 K and flow rates between 20 and 80 mL/min. The presence of CO_2 does not seem to influence the intracrystalline transport rate of the investigated light hydrocarbons (*n*-C_4 and *n*-C_6). On the other hand, the situation for *n*-C_8 and *n*-C_{10} is more complex. The diffusivity values are higher compared to the previously reported values.

Keywords Diffusion · Paraffins · Carbon dioxide · Silicalite · ZLC

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1 Introduction

Zero Length Column (ZLC) is a powerful chromatographic technique for diffusivity measurements of pure gases on porous solids (Eic and Ruthven 1988). It is performed by loading a small amount of adsorbent with a diluted mixture of adsorbate until equilibrium in the adsorbed phase is reached. After that, the inlet valve is switched to allow an inert stream to clean the adsorbent. A desorption curve is obtained and from it the diffusivity can be extracted. The advantage of this method is the elimination of external mass- and heat-transfer resistances by the use of low adsorbate concentrations, very small adsorbent sample amounts as well as high carrier flow rates during desorption. It has been extensively used for diffusivity measurements in zeolites and other molecular sieves (Cavalcante et al. 2000, 2003; Grande et al. 2003, Qiao and Bhatia 2005, Huang et al. 2008, Lima et al. 2008) and to study diffusion in biporous materials (Brandani 1996), under non-linear conditions (Brandani et al. 2000), tracer diffusion (Brandani et al. 1995) and liquid systems (Brandani and Ruthven 1995).

Although several research works on the subject of diffusion in MFI zeolites are available in literature (Kärger et al. 1982; Hayhurst and Paravar 1988; Eic and Ruthven 1989; Shen and Rees 1991; Hufton and Ruthven 1993; Cavalcante and Ruthven 1995; Vroon et al. 1996; Talu et al. 1998; Webb et al. 1999; Jobic 2000; Jiang and Eic 2003; Zhu et al. 2001, 2004; Koriabkina et al. 2005; Möller et al. 2009), there is still a number of open questions including the real intracrystalline diffusivities in silicalite-1/ZSM-5 (Kärger 2003). Zeolites of MFI type possess channels defined by 10-membered oxygen rings with a diameter of 5.5 Å, which can be used to separate gases on a scale of molecular sieving. The intracrystalline diffusivity of the molecular species involved in this process is often the rate controlling factor.

Therefore it is important to investigate the transport properties of paraffins in these materials.

On the other hand, the most practical applications of zeolites involve binary or multi-component diffusion. However, few literature data are available for binary mixture systems.

In this study, the diffusion of linear paraffins with different carbon numbers in silicalite has been measured by zero length column (ZLC) method. In order to investigate the influence of carbon dioxide (CO_2) adsorption on diffusion properties, a series of experiments was performed involving hydrocarbons mixed with CO_2.

2 Mathematical model

The mathematical modeling of the ZLC technique is based in the following assumptions: spherical adsorbent particles, Fickian diffusion, linear sorption isotherm, perfect mixing through the cell, isothermal conditions, high flow rate of the gas stream and neglect of the hold-up in the fluid phase.

With these assumptions, the response curve is given by Crank (1979):

$$\frac{c}{c_0} = 2L \sum_{n=1}^{\infty} \frac{\exp\left(-\frac{\beta_n^2 Dt}{R^2}\right)}{[\beta_n^2 + L(L-1)]} \tag{1}$$

where β_n are the roots of (2):

$$\beta_n \cot \beta_n + L - 1 = 0 \tag{2}$$

and

$$L = \frac{1}{3} \frac{FR^2}{KV_s D} \tag{3}$$

In these equations, c is the concentration at any time t, c_o is the initial concentration, F is the purge flow rate, V_s is the crystal volume, K is the dimensionless Henry law constant, D is the diffusion coefficient and R is the particle radius (L and β_n are dimensionless parameters).

In the long time region (data from the tail of the desorption curve) (1) reduce to simple exponential decay curves since only the first term of the summation is significant. A plot of $\ln(C/C_0)$ vs. t should therefore present a linear asymptote, in the long time region. The slope and intercept of the linear asymptote allow the calculation of the parameters D and L.

3 Experimental

A schematic description of the ZLC apparatus is presented in Fig. 1. In the ZLC experiment a small sample of the adsorbent is equilibrated with an inert carrier gas stream containing a small concentration of an adsorbing component. At time zero the flow is switched to a pure carrier stream and the adsorptive effluent concentration is monitored using an appropriate detector. The zero length column (packed with 2 mg of zeolite) is placed between two sintered disks in a 1/8-in stainless steel Swagelok union inside a GC oven (Chrompack CP9001 Gas chromatograph). Measurements were carried out using silicalite-1 which is composed of sinusoidal pores in the x-direction and straight channels in the y-direction. Both pores are roughly 5.5 Å in diameter. The concentration of the effluent species was measured with a flame ionization detector (FID). Before starting an experiment, the zeolite was activated by heating in a high-purity carrier stream (He or Ar) from room temperature to

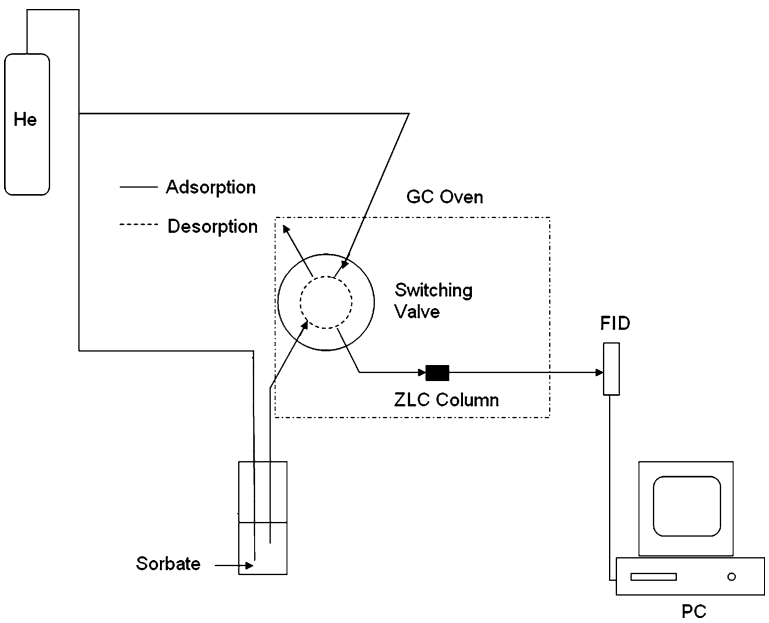

Fig. 1 Schematic of ZLC apparatus

423 K overnight. The sorbates used were a series of linear alkanes (*n*-butane, *n*-hexane, *n*-octane and *n*-decane), 99% purity, purchased from Merck. Helium, argon and CO_2 from Linde with a purity of 99.99% was used as carrier gas.

4 Results and discussion

4.1 Effect of the purge flow rate on diffusion coefficients

The ZLC measurements were performed for systems involving *n*-C_4, *n*-C_6, *n*-C_8 and *n*-C_{10} under helium purge flow rate varying from 40 mL/min to 80 mL/min. The diffusional time constants were obtained from the simultaneous analysis of two response curves at different flow rates. In the case of kinetics control, these desorption curves should be nearly parallel to each other at the long time region indicating that the intracrystalline diffusivity is independent of the flow rate. Figure 2 shows desorption curves of the typical shape expected for a diffusion-controlled process. These curves exhibit an initial drop in concentration corresponding to the fast purging of the system free volume followed by a slower exponential decay. This means that the sorbate removal rate from the crystals into the purge gas is slow and micropore diffusion resistance is significant. In Table 1 a summary of the experimental results is given for all sorbates that were studied. As expected the diffusivity value (D) is independent from the purge flow and the value of the ZLC parameter L is proportional to the purge flow rate (see (3)).

The value of L can be also used to determine whether the transport process is controlled by equilibrium or kinetics effects. According to Hufton and Ruthven (1993), the transport process is controlled by equilibrium if $L < 1$. For $L > 10$ the process is controlled by the kinetics of the system. At $L = 5$ occurs the transition point from equilibrium-controlled to the kinetics-controlled process. The obtained values for L presented in Table 1 (except for *n*-butane with flow rate 20 mL/min) are larger than 10, indicating that the overall transport of sorbate molecules is mainly due to a kinetic controlled process. In the case of the experiment for *n*-butane with the lower flow rate (20 mL/min, for which $F = 5$), the desorption curve shows an essentially linear decrease of $\ln(C/C_0)$ with time from the beginning of the process (Fig. 6a). This suggests that the desorption process in this case may be equilibrium controlled, as the low F value indicates. Nevertheless, the diffusivity values thus derived are in good agreement with the value for the experiment with flow rate of 40 mL/min (for which $F = 34$). Furthermore, earlier reported diffusivities for *n*-butane in MFI zeolites (Hufton and Ruthven 1993; Jiang and Eic 2003), using the ZLC method, yielded values with the same order of magnitude of our values (ca. 10^{-12} m^2/s). These authors have also reported that their measurements for *n*-butane in silicalite could have been equilibrium controlled despite having used larger flow rates than those we used in our experiments.

Figure 3 shows experimental desorption curves (*n*-decane at 303 K) together with the theoretical curves predicted according to (1). The parameters D/R^2 and L were derived from the experimental curves, via long time method, as shown in Table 1. Good agreement is observed between experiment and theory.

4.2 Effect of dead volume and purge gas

The ZLC theory assumes that external film mass transfer is fast enough to ensure that the sorbate concentration is the

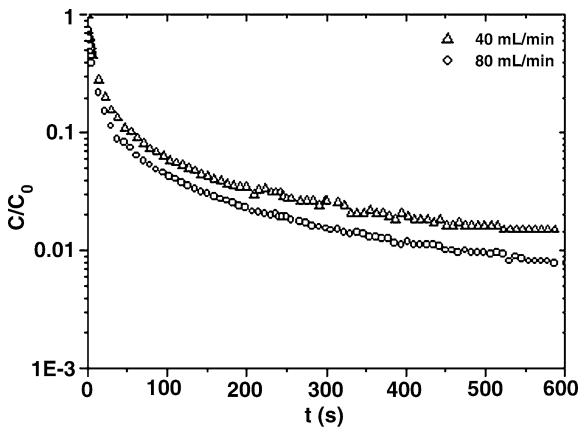

Fig. 2 Desorption curves for *n*-octane on silicalite-1 at 303 K at different flow rates (△ 40 mL/min; ○ 80 mL/min)

Table 1 Diffusion coefficients of the corresponding paraffins in silicalite at 303 K

Adsorbate	with He			with CO_2		
	F (mL/min)	L	$D \times 10^{13}$ (m^2/s)	F (mL/min)	L	$D \times 10^{13}$ (m^2/s)[a]
n-C_4	20	5	16.0	20	5	16.3
	40	34	15.2	40	40	
n-C_6	40	14	5.6	20	10	5.1
	80	23	6.3	40	18	
n-C_8	40	67	3.1	20	18	4.5
	80	120	3.2	40	30	
n-C_{10}	40	109	1.6	20	11	4.5
	80	300	1.7	40	29	

[a]Average values for $D \times 10^{13}$ (m^2/s) obtained by desorption curves at two different flow rates (20 mL/min and 40 mL/min)

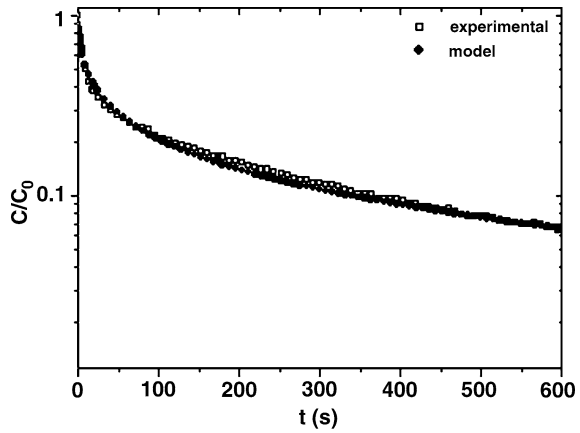

Fig. 3 Comparison between experimental and theoretical desorption curves for *n*-decane at 40 mL/min and 303 K. Theoretical line is calculated from equations (1)–(3) with parameters given in Table 1

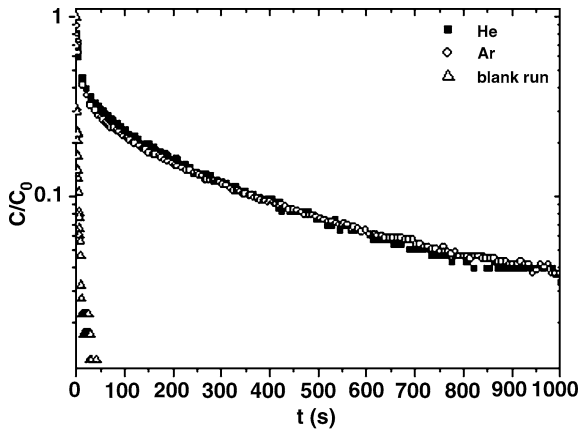

Fig. 4 Experimental ZLC desorption curves for *n*-decane at 303 K showing the comparison between measurements with helium and argon as carrier gas and curve for blank run. Flow rate: 40 mL/min

same in the bulk gas and at the crystal surface. The validity of this assumption may be conveniently verified by using different purge gases (He and Ar) having different molecular diffusivities. If the mass transfer rate is controlled by intracrystalline diffusion, desorption curves measured under similar conditions with different purge gas, should be identical (Eic and Ruthven 1988). This way, the absence of significant extracrystalline resistance to mass transfer was confirmed by comparing replicate desorption curves for *n*-decane obtained with helium and argon carrier gas, as show in Fig. 4. It can be seen that desorption curves are independent of the gas.

In order to investigate the effect of dead volume, a blank experiment was carried out in the absence of adsorbent sample. The curve is also shown in Fig. 4. In the blank response, C/C_0 falls to 10^{-2} in about 30 s, whereas the typical run shows a very slow concentration decay over a time range of more than 1000 s.

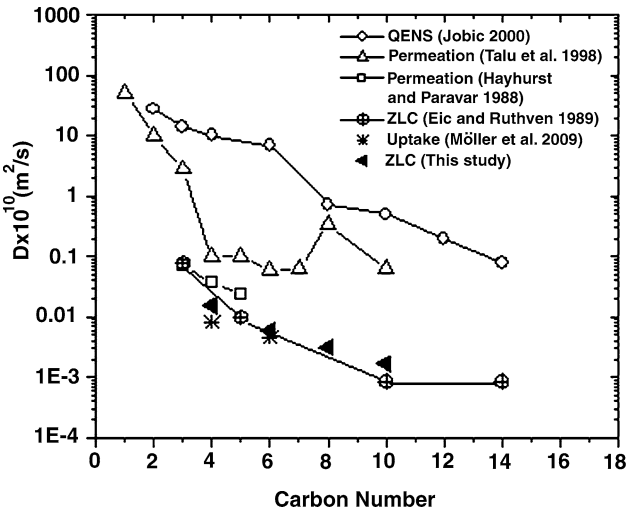

Fig. 5 Diffusion coefficients for *n*-alkanes in MFI zeolites at 303 K obtained through different methods. Note: permeation data from Hayhurst and Paravar (1988) were obtained at 334 K

4.3 Effect of the carbon number of linear paraffins

From Table 1, one can notice that the diffusivity of *n*-alkanes decays essentially with increasing chain length. This is typically observed for diffusivity of linear paraffins with carbon number for several systems (Kärger and Ruthven 1992). However, deviations of this pattern can also be found in the literature, like for diffusion of linear paraffins in 5A zeolite which show a strong increase above *n*-C_8 and a maximum between *n*-C_{10} and *n*-C_{14} (Jobic et al. 2003).

Intracrystalline diffusion of *n*-alkanes in MFI zeolites has been widely studied by several methods, as presented in Fig. 5. The diffusivity data obtained in this study were consistent with the results of earlier ZLC measurements and showed the same previously observed disagreement with other reported techniques. However, it is important to note that all techniques, with the exception of the permeation results from Talu et al. (1998), exhibit a steady decrease of diffusivity values with increasing carbon number. We may also observe that earlier permeation diffusivity data (Hayhurst and Paravar 1988) showed in general good agreement with the diffusivity values derived from the ZLC measurements. Furthermore, recent uptake measurements with non-isothermal modeling of the experimental data (Möller et al. 2009) also show reasonable agreement with the ZLC results.

This discrepancy cannot be attributed to the presence of extracrystalline resistance, because this can be excluded by varying the carrier gas and the purge rates. Indeed, the apparent difference between the results from different techniques is a matter still under investigation in the field of diffusion in zeolites. Kärger (2003) reported that the diffusivity may most decisively depend on the relevant space and time scales of observation as well as on the physical state under which the measurements are carried out.

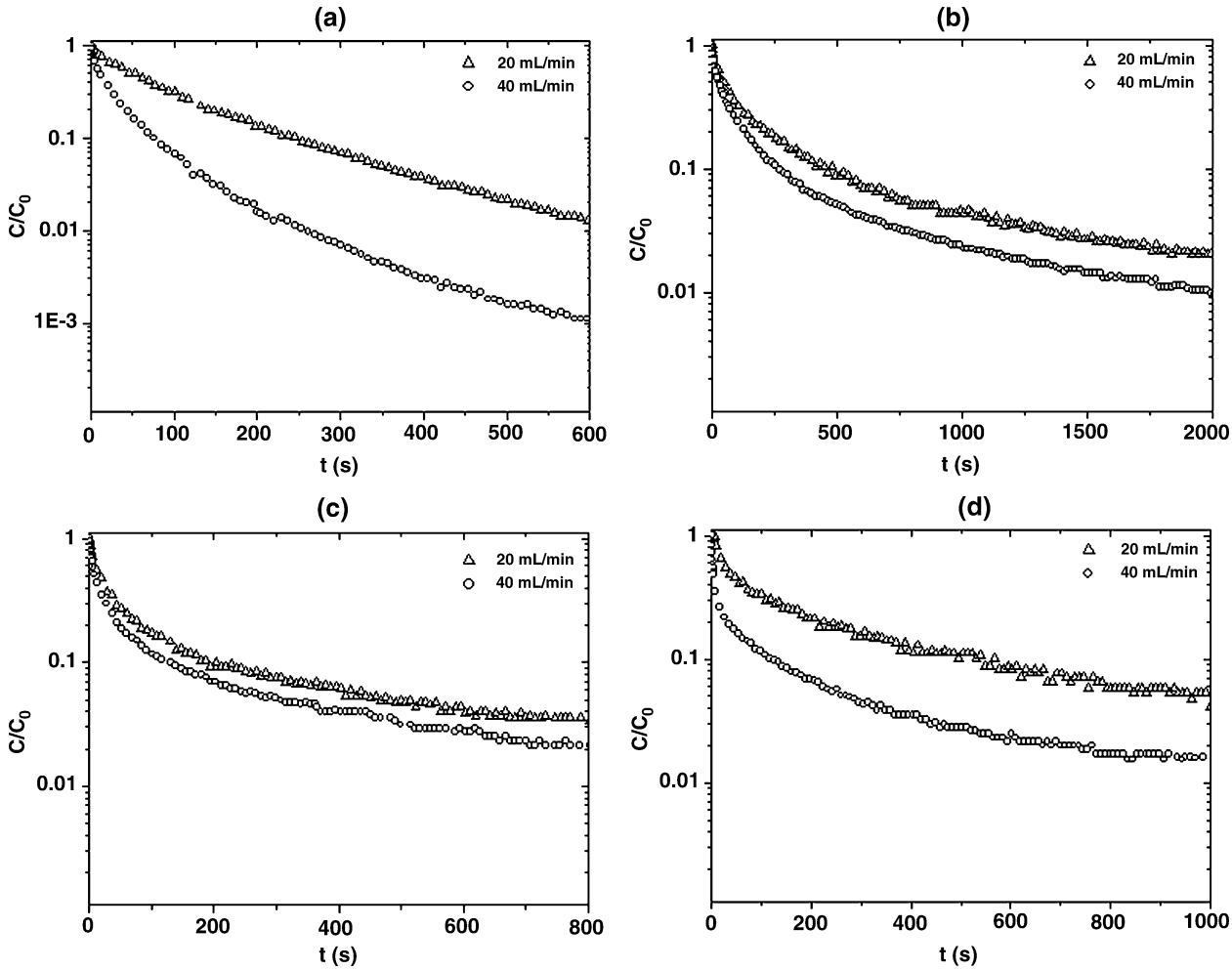

Fig. 6 Experimental ZLC curves on silicalite-1 at 303 K for n-C_4 (**a**), n-C_6 (**b**), n-C_8 (**c**), n-C_{10} (**d**) in the presence of CO_2

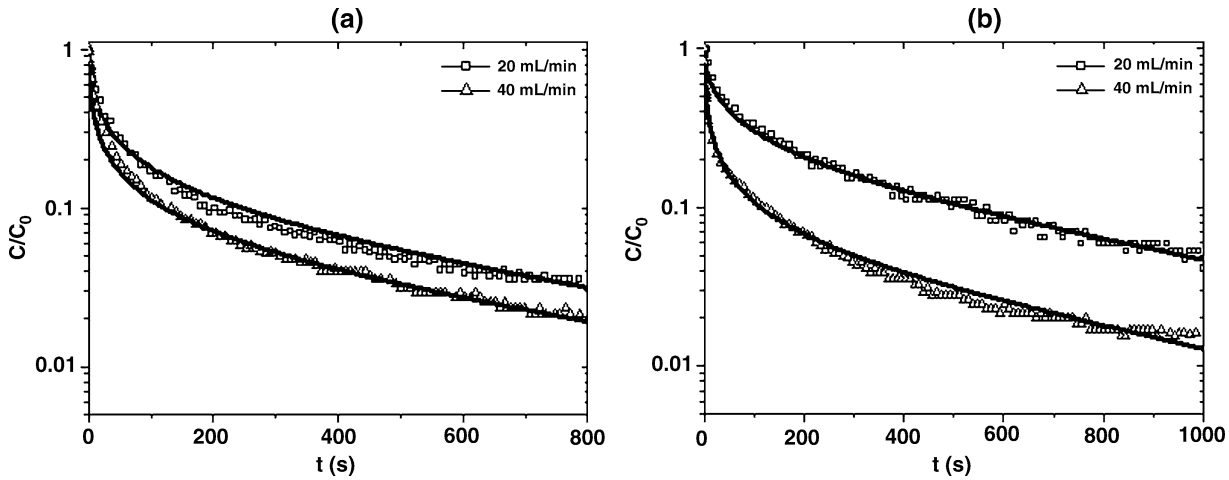

Fig. 7 Experimental and theoretical curves for the systems n-C_8/CO_2 (**a**) and n-C_{10}/CO_2 (**b**)

4.4 Diffusion of linear paraffins in CO_2 carrier gas in silicalite

The ZLC experimental procedure for linear paraffins in a CO_2 carrier gas is similar to that described for the measurements carried out with helium and argon. Figure 6 shows desorption curves obtained with different flow rates. The desorption curves are parallel to each other, like in the case of He carrier gas.

The curve for n-C_4 in Fig. 6 reveals that the initial decrease in C/C_0 seems to be linear with time. This suggests fast diffusion rates. According to Hufton and Ruthven (1993), if the intracrystalline transport is fast compared to the removal rate of sorbate by the purge gas, the desorption process may be influenced by equilibrium effects.

The same mathematical model was used for the evaluation of the diffusion coefficients from these response curves. The obtained parameters are listed in Table 1 and were used to calculate the theoretical desorption curves, as shown in Fig. 7 (systems n-C_8/CO_2 and n-C_{10}/CO_2).

The diffusivity values (Table 1) obtained for n-C_8 and n-C_{10} under CO_2 carrier can be considered essentially the same and seem to be higher compared to the values found before using helium as carrier gas (Fig. 8).

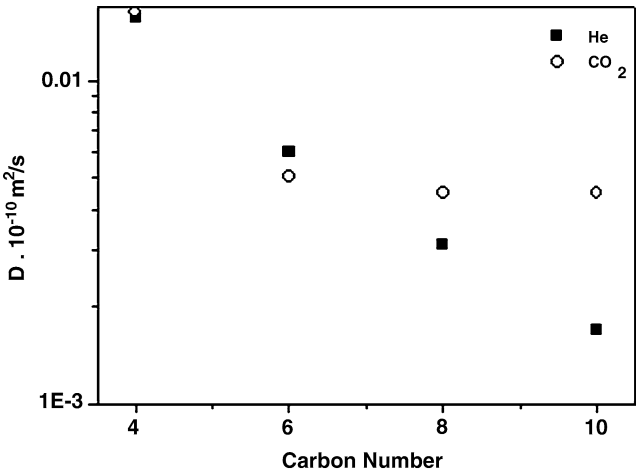

Fig. 8 Comparison between diffusion coefficients for n-alkanes (desorbed with a helium purge) and n-alkanes/CO_2 in silicalite

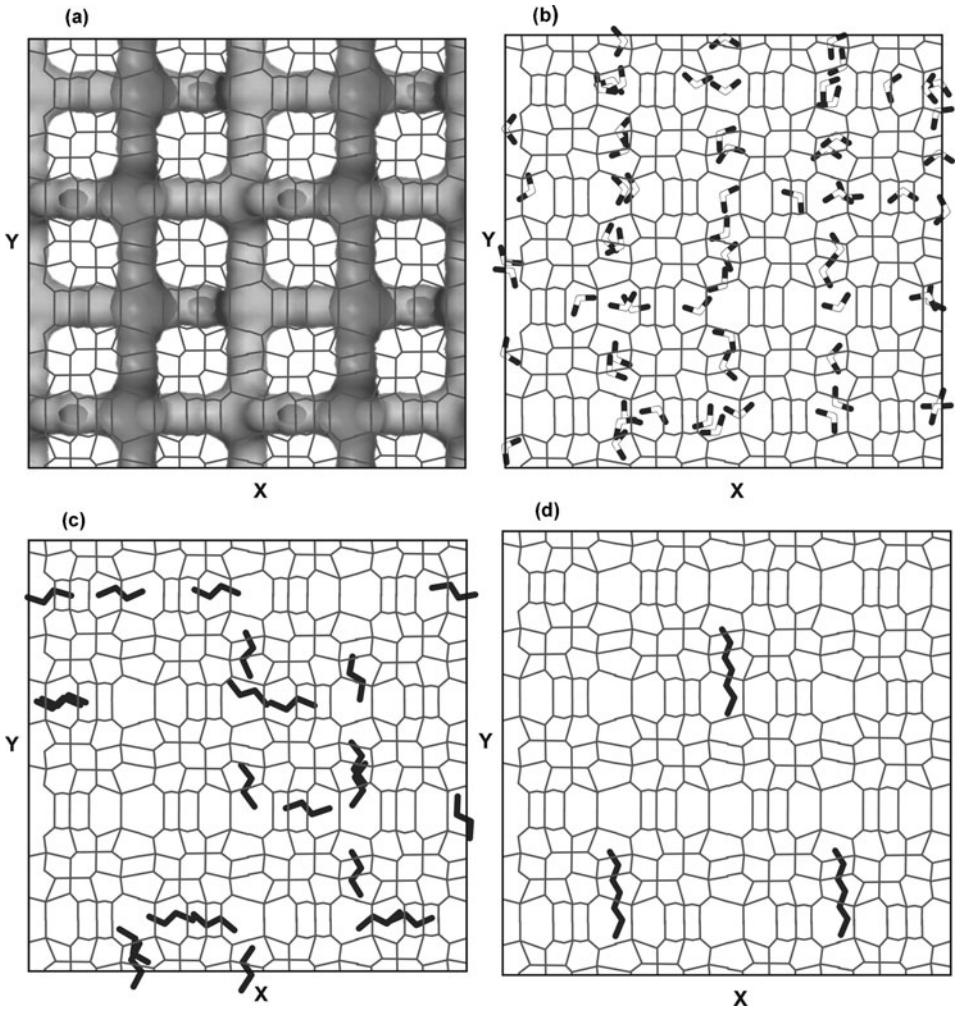

Fig. 9 Schematic view of MFI framework and molecules positioning. (**a**) MFI framework: straight channels (perpendicular to x-axis) and zig-zag channels (parallel to x-axis); (**b**) Positioning of CO_2, predominantly in straight channels; (**c**) Positioning of n-C_4, predominantly in zig-zag channels; (**d**) Positioning of n-C_7, predominantly in straight channels

The diffusion coefficients of light alkanes (n-C_4 and n-C_6) do not seem influenced by the presence of CO_2. On the other hand, it can also be observed in Fig. 8 that the diffusion of slower moving species (n-C_8 and n-C_{10}) may be affected by the presence of CO_2. The influence of carbon dioxide adsorption on hydrocarbons diffusion properties, especially for heavier molecules, needs further investigation. We propose a possible explanation for this behavior in the following section.

4.5 Competition between the linear paraffins and CO_2 in silicalite adsorption

It has been established by Chempath et al. (2004) that linear paraffins up to C_5 had preference to locate in the zig-zag channels of silicalite, whereas molecules with higher carbon numbers (more than 6) would prefer the straight channels. Recent simulations by Yue and Yang (2006) have demonstrated that the CO_2 molecules also prefer the straight channels of silicalite. So the CO_2 molecules would not compete with the low carbon number paraffins since they prefer to sit in different sites within the silicalite framework. However, for the higher carbon numbers, they will be competing for the same straight channels with CO_2, and thus these larger paraffins will probably tend to diffuse faster through the crystal when in the presence of CO_2 than when in the presence of He (which does not compete for adsorption sites). A schematic view for the proposed locations of the paraffins (lower and higher carbon numbers) and CO_2 in the silicalite structure is depicted in Fig. 9.

5 Conclusion

The ZLC method was applied to study the kinetic behavior of linear paraffins in silicalite-1 with different carrier gases. It was found that the desorption process of paraffins in silicalite-1 is attributed to micropore diffusion. The obtained diffusion coefficients agree well with previous ZLC data (Eic and Ruthven 1989).

The presence of CO_2 does not seem to influence the intracrystalline transport rate of the investigated light hydrocarbons (n-C_4 and n-C_6) in silicalite. However, for n-C_8 and n-C_{10} the behavior was different. The diffusivities are higher than the obtained values by desorption with helium (or argon) purge.

Acknowledgements This work was performed within the scope of a cooperation program between Brazil and Germany (PROBRAL/CAPES/DAAD) and the authors acknowledge financial support from Conselho Nacional de Desenvolvimento Científico e Tecnológico—CNPq (Brazil), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior—CAPES (Project Number 227/06; Brazil) and Deutscher Akademischer Austausch dienst—DAAD (Project Number 415-br-probral/po-D/05/30378; Germany).

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