Kinetics of adsorption of pure and mixtures of linear and branched C6 alkanes onto silicalite by non-equilibrium molecular dynamics.

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The separation of saturated branched and linear alkanes may be investigated by selective adsorption on microporous organophilic MFI type zeolite. From the literature, adsorption equilibria of mixtures show a favourable selectivity for less branched alkanes [1]. However the separation process is significantly influenced by the transport properties. The knowledge of the transport coefficients of alkanes in the zeolite is then useful to optimize the separation process. The literature values of intracrystalline diffusion coefficients of hydrocarbons in MFI type zeolite are spread over a wide range of order of magnitude [2]. They depend on the experimental techniques, origin of zeolites… In this study we investigated kinetics of adsorption of n-hexane (HEX) and 2 methyl-pentane (2MP) on aggregates and infinite membrane of silicalite at a temperature of 440K using transient non equilibrium molecular dynamics simulations (TNEMD) [3]. This type of simulation gives access both to the kinetics of adsorption and to the equilibrium state. In a recent article [3] we presented a TNEMD study of the adsorption kinetics of n-butane on aggregates of silicalite. The same procedure is applied for HEX and 2MP on aggregates and extended to the study of infinite membranes to get both the Fick's diffusion coefficients and the self-diffusion coefficients along the three crystallographic orientations. In the following, the directions *a, b* and *c* will refer to the crystallographic directions respectively [100], [010], [001] commonly used for the MFI type zeolite [3]. *b* is the direction of the straight channels, *a* and *c* are in the direction of zigzag channels. Details of the simulations are described in ref. [3].
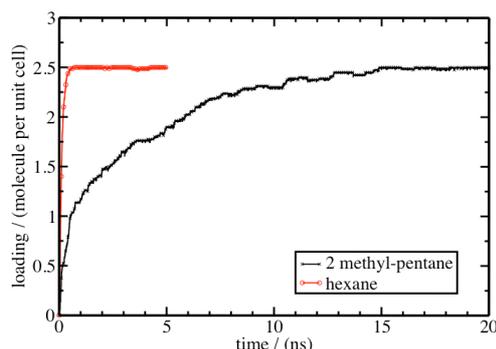
Figure 1: Comparison of the kinetics of adsorption of pure n-hexane and 2methyl-pentane in a membrane of zeolite silicalite. The external surface is perpendicular to the straight channel.

In figure 1 the kinetics of adsorption of HEX and 2MP in a membrane of silicalite are compared. Hex reaches equilibrium in less than 1ns while it is achieved in about 15 ns with 2MP. The averaged simulated Fick's and self-diffusion coefficients are stored in table 1. In agreement with figure 1, they are higher for HEX than for 2MP by about a factor 100. As expected, the self-diffusion coefficients show a preferential mobility of the molecules along the straight channels (direction b) then along a and finally along c directions, a, b and c being the crystallographic direction. This trend agrees with the simulated results of Fick's diffusion coefficient for 2MP. This suggests that kinetics process is well governed by intracrystalline diffusion for 2MP.

For HEX, the Fick's diffusion coefficient is higher in a direction. The comparison with self-diffusion coefficients and additional analysis on uptake adsorption curves shows that kinetics is not governed by intracrystalline diffusion at least in directions a and b. As obtained for n-butane [3], other phenomena like transport in the gas phase or/and mass transfer through the external surface are probably involved.

		$D/(m^2.s^{-1})$	
	Techniques	2MP	HEX
D_{Fick} TNEMD	Aggregate	$1.8\ 10^{-11}$	$4.1\ 10^{-10}$
	a	$1.2\ 10^{-10}$	$1.3\ 10^{-8}$
	b	$2.3\ 10^{-10}$	$8.4\ 10^{-9}$
	c	$5.2\ 10^{-12}$	$4.2\ 10^{-9}$
	Average abc	$1.2\ 10^{-10}$	$8.7\ 10^{-9}$
D_{self} EMD	a	$2.3\ 10^{-11}$	$1.8\ 10^{-9}$
	b	$2.9\ 10^{-11}$	$3.8\ 10^{-9}$
	c	$3.1\ 10^{-12}$	$4.2\ 10^{-10}$
	Average abc	$1.8\ 10^{-11}$	$2.0\ 10^{-9}$

Table 1: Self and Fick's diffusion coefficients of 2MP and HEX adsorbed on MFI type zeolite by equilibrium molecular dynamics (EMD) and TNEMD.

An additional simulation of an equimolar mixture of HEX and 2MP shows surprisingly that the kinetics of adsorption of HEX is not perturbated by the presence of the other compound while the kinetics of 2MP is much slower. The selectivity here favours the linear compound, at short time and decreases with time. As the loading of 2MP increases, a displacement of HEX by 2MP is observed.

references
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[3] J.-M. Simon, A. Decrette, J.-P. Bellat, J. M. Salazar, Mol. Sim. 30 (2004) 621.