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Kinetics of Adsorption of Linear and Branched C6 Alkanes onto ZSM-5 Zeolite - Experiments and Molecular Simulations

Jean-Marc Simon, Edith Fardet-Lemaire, Igor Bezverkhyy,
Jean-Pierre Bellat, Florence Baras
Laboratoire de Recherches sur la Réactivité des Solides, UMR 5613 CNRS, Université de Bourgogne, 9 avenue A. Savary, BP 47870, 21078 Dijon, France,
E-Mail: jmsimon@u-bourgogne.fr

1. Introduction

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 orders of magnitude [2]. They depend on the experimental techniques, origin of zeolites… The use of these values may be then difficult and even questionable. The aim of this work is to compare transport coefficients determined by two transient macroscopic experiments, the manometry and the "Zero Length Column" chromatographic method (ZLC), and by Molecular Dynamics simulations at Equilibrium (EMD) and out of equilibrium using a Transient Non-Equilibrium (TNEMD) approach [3]. The diffusion of n-hexane (HEX) and 2-methylpentane (2MP) in ZSM5 zeolite (Si/Al ratio =500) prepared by Degussa is studied at 443 K and at low loadings (N^a<1molec.uc^{-1}). For molecular simulations pure siliceous silicalite-1 with orthorhombic structure is used. The experimental techniques are well described elsewhere [2].

		D/(m^2.s^{-1})	
	Techniques	2MP	HEX
D_{Fick} Exp.	Manometry	3.6 10^{-13}	2.7 10^{-13}
	ZLC	4.5 10^{-12}	5.1 10^{-12}
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}

Tab. 1: Self- and Fick's diffusion coefficients of 2MP and HEX adsorbed on MFI type zeolite by different methods.

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 [100], [010], [001] respectively 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].

2. Results

The transient methods provide kinetics of adsorption (manometry, TNEMD) and desorption (ZLC) uptake. Results were analyzed by integrating analytically the Fick's law of diffusion [2]. Within the assumption that the mass transfer in micropores governs kinetics, this procedure leads to values of the intracrystalline Fick's diffusion coefficients. The simulated self-diffusion coefficients were directly calculated by using the well-known Einstein's relation at equilibrium (EMD).

Table 1 summarizes the self- and Fick's diffusion coefficients obtained by the four different approaches. Each kind of experiment gives identical values for 2MP and HEX within the statistical uncertainties. However, the results obtained by ZLC are one order of magnitude higher. In contrast the averaged simulated Fick's and self-diffusion coefficients are higher for HEX than for 2MP by about a factor 100. Moreover, these values are higher than the experimental ones. The self-diffusion coefficients, as expected, show a preferential mobility of the molecules along the straight channels (direction *b*), then along *a* and finally along *c* directions. This trend agrees with the simulated results of Fick's diffusion coefficient for 2MP. This suggests that kinetics is well governed by intracrystalline diffusion for 2MP. The shifts of one order of magnitude are then attributed to thermodynamic factors relating both kinds of coefficients [2]. 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 show 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. Despite the differences of scales in time and space between simulations and experiments, results indicate that for both HEX and 2MP, experimental kinetics is limited by other phenomena than intracrystalline diffusion.

3. Conclusion

The aim of this work was to compare kinetics of adsorption of n-hexane and 2-methylpentane on ZSM-5 by different approaches, ZLC and manometry and molecular dynamics under equilibrium and out of equilibrium at 443 K. Results show that experiments give no direct access to intracrystalline diffusion. Mass transfer in the gas phase and through the external surface seem to play a major role in the adsorption process.

references

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