diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Kinetic Monte Carlo Study of Binary Diffusion in MFI-Type Zeolite

Nicolas Laloué(1,2), *Catherine Laroche*(1), *Hervé Jobic*(2), *Alain Méthivier*(1)

(1)Institut Français du Pétrole, BP 3, 69390 Vernaison, France

(2)Institut de Recherche sur la Catalyse, 2 avenue A. Einstein, 69626 Villeurbanne, France

E-Mail: catherine.laroche@ifp.fr

1. Introduction

Separation induced by kinetic effects has been investigated, using zeolites as a shape selective adsorbent [1]. The control of diffusion process, requiring a precise knowledge of self-, transport and corrected diffusivities (D_{self}, D_t and D_C, respectively) of molecules inside the nanoporous material, is essential for the design of industrial applications. In the case of strongly-binding or tight-fitting guest-zeolite systems, residence times in adsorption sites are much longer than travel times between sites so that diffusion becomes a slow activated process. Diffusion can then be viewed as successive random jumps from an adsorption site to another by crossing free energy barriers. Combining Kinetic Monte Carlo (KMC) algorithm and lattice model is the most adapted technique to study diffusion at finite loadings of poorly connected systems [2]. By its flexibility, it allows to consider different type of sites and to account for their local environment.

In this work, we report a study of the loading dependence of single-component diffusion of linear hexane (nC6) and of binary diffusion of nC6 and 2,2-dimethylbutane (22DMB) mixture in MFI-type zeolite at 300K, using a lattice model approach combined with KMC.

2. Kinetic Monte Carlo Simulation

In this study, the silicalite framework is represented as a three-dimensional network of intersecting straight (str) and zigzag (zz) channels. Molecules are randomly positioned on the lattice and can move from one site to the neighbouring site via hops, with a probability determined by transition rates estimated by *ad hoc* atomically detailed simulations [3,4]. Local molecular interactions are taken into account by modifying the magnitude of the free energy barrier according to the methodology developed by Reed and Ehrlich [5] and adapted for KMC applications with the introduction of a parameter f [6]. A standard KMC algorithm with variable time step is implemented to propagate the system. D_{self} is determined using the Mean Square Displacement (MSD) of the N individual particles. D_C, also called Maxwell-Stefan diffusivity, is related to the displacement of the centre of mass of the N adsorbed particles. MSD calculations are performed using the order-n algorithm [7,8], mapping the variable time scale on a periodic time scale as done in Molecular Dynamics simulations. The source code developed here has been validated by quantitatively reproducing the results of the loading dependence of D_{self} and D_C of CH_4 in MFI on cubic and MFI lattices [6].

The loading dependence of single-component diffusion of nC6 in silicalite at 300K, has been investigated using a KMC model based on original anisotropic transition rates. In order to account for the molecule distribution within the zeolite framework, two different approaches have been developed to this model enclosing adsorption features via the introduction of the Langmuir constants of the DSL model. Moreover, guest-guest interactions are accounted for. The results of these KMC simulations for one of the approach developed are in good agreement with recent experimental QENS measurements [9], for both D_{self} and D_C.

The KMC model used for the study of binary diffusion at 300 K of nC6 and 22DMB mixture in silicalite is based on information coming from the single component investigation and accounts for the different saturation capacities of both species. It also allows for all type of molecular interactions to be considered by introducing f_{ij} parameters. As this model only accounts for nearest neighbours influence, the interactions between molecules of 22DMB are neglected. Results have shown a larger impact of interaction between linear and double-branched molecules than interactions between two linear molecules. Besides, the presence of 22DMB molecules in intersection sites has a significant impact on nC6 self- and corrected diffusivities compared to its behaviour as a single component. Near $\Theta_{22DMB,sat}$, the nC6 diffusivities sharply decrease towards 22DMB diffusivity values due to the reduction of vacant intersection sites.

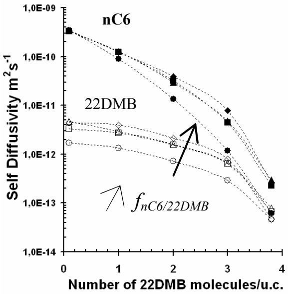

Fig. 1: 22DMB loading dependence of self-diffusion of nC6 and 22DMB.

3. Conclusion

Kinetic Monte Carlo combined with a lattice model approach is used to simulate single-component and binary diffusion in an MFI-type zeolite. A good agreement is obtained with experimental behaviours of D_{self} and D_C for nC6 diffusion. The binary diffusion study shows the impact of inter-species interaction, as well as site blocking effect. Deceleration/acceleration effect on molecules has also been confirmed.

References

[1] Cavalcante C.L.J., Ruthven D.M., Ind. Eng. Chem. Res. 34 (1995) 185-191.
[2] Keil F.J., Krishna R., Coppens M.O., Rev. Chem. Eng. 16 (2000) 71-197
[3] June R.L., Bell A.T., Theodorou D.N., J. Phys. Chem. 95 (1991) 8866-8878
[4] Dubbeldam D., Beerdsen E., Vlugt T.J.H., Smit B., J. Chem. Phys. 122 (2005) 224712
[5] Reed A.D., Ehrlich G., Surf. Sci. 102 (1981) 588-601
[6] Krishna R., Paschek D., Baur R., Microporous and Mesoporous Mater. 76 (2004) 233-246
[7] Frenkel D., Smit B., "Understanding Molecular Simulations : From Algorithms to Applications", 2nd Ed, Academic Press, San Diego, USA (2002)
[8] Auerbach S.M., Henson N.J., Cheetham A.K., Metiu I.H., J. Phys. Chem. 99 (1995) 10600-10608.
[9] Jobic H., Laloué N., Laroche C., van Baten J.M., Krishna R., J. Phys. Chem. B 110 (2006) 2195-2201.