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Mixture Diffusion in Silicalite-1 Studied by MAS PFG NMR

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1. Introduction

The application of solid state MAS NMR in combination with pulsed field gradients opens new possibilities for measuring multi-component diffusion in nanoporous materials, especially in zeolites [1]. These options are related to an enhancement of the sensitivity with respect to smaller molecular displacements, and to an increased spectral resolution, which allows selective diffusion measurements from different components. Both options are illustrated by measuring the diffusion coefficient of different molecular mixtures adsorbed in zeolite silicalite-1.

2. Selective diffusion measurements of binary mixtures absorbed in silicalite-1

In general, NMR spectra of polycrystalline materials are broadened by anisotropic interactions such as dipolar coupling, chemical shift anisotropy, quadrupolar coupling, and susceptibility effects. Depending on their strength and the achievable rotation frequency, MAS can reduce or even completely remove these broadenings of the NMR signals. Magic-angle spinning and pulsed field gradient NMR have been combined to study the intracrystalline diffusion of mixtures in the zeolites material. This new method allows high resolved spectra and enabled selective diffusion measurements of species with chemical shift differences of less than 0.1 ppm. This contribution presents an NMR diffusometry study of n-butane/isobutane and n-butane/methane mixtures absorbed in MFI type zeolite.

The diffusion coefficient of n-butane mixed with isobutane in silicalite-1 was studied in dependence on the partial concentration [2]. It was found that n-butane diffusivity decreases with increasing amount of isobutane, and presents one step or discontinuity at about 0.5 n-butane molecules per channel intersection. Further on, with decreasing

content of n-butane (increasing content of isobutane) the diffusivity of n-butane drops exponentially, with the value extrapolated to zero loading of n-butane coinciding with the isobutane diffusivity. Diffusion coefficients for isobutane in silicalite-1 could be measured for the first time by NMR diffusometry. The obtained values are 1.63×10^{-12} m^2s^{-1} and 2.32×10^{-12} m^2s^{-1} at 300 K and at 363 K, respectively.

The experimental results were simulated by Configurational-Bias Monte Carlo (CBMC). The simulation have shown that while n-butane can be located along either straight or zig-zag channels of silicalite-1, isobutane is preferentially located at the intersections, because of configurational considerations. Diffusivity of isobutane is about two to three orders of magnitude lower than that of n-butane. Consequently, the occupation of the intersections of the channels by isobutane is tantamount to blockage, leading to severe reduction in the molecular traffic of the more mobile n-butane along the straight channels in the *y*-direction.

Diffusivity properties of one n-butane/ methane equimolar mixtures were also studied. The diffusion coefficient of both components was determined in dependence on the diffusion time and the temperature.
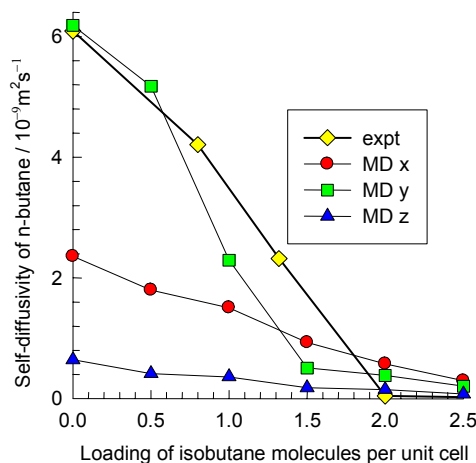

Fig.1 Experimental and MD simulation results of self-diffusivity of n-butane in mixtures of n-butane and isobutane at 363 K in silicalite-1. The total loading is maintained at 4 molecules per unit cell.

3. Conclusion

Magic-angle spinning and pulsed field gradient NMR have been combined to study the intracrystalline diffusion of molecular mixtures in the zeolite silicalite-1. In this way, detrimental line broadening due to inevitable susceptibility heterogeneities in silicalite-1 which so far has prohibited highly resolved measurements has been dramatically reduced. MD simulations are in qualitative agreement with the experimental data for silicalite-1; the sharp decline in the self-diffusivity of n-butane with increased isobutane loadings is a consequence of the blockage of the intersections by the tardy isobutane molecules.

References

[1] A. Pampel, M. Fernandez, J. Kärger, D. Freude, Chem. Phys. Lett. 407 (2005) 53–57
[2] M. Fernández, J. Kärger, D. Freude, A. Pampel, J. M. van Baten, R. Krishna, Microporous and Mesoporous Materials. (submitted)