Self-diffusion of *n*-alkanes in MFI-type zeolites: A Molecular Dynamics study and a comparison to Quasi-Elastic Neutron Scattering experiments.

F.H.R Leroy[1,#,], H. Jobic[2], B. Rousseau[1] and A.H. Fuchs[1]*

[1]Laboratoire de Chimie-Physique, Université Paris-Sud, 91405 Orsay, France, [2]CNRS-Institut de Recherche sur la Catalyse, 2, avenue Albert Einstein, 69926 Villeurbanne, France, *current position Universitat Rovira i Virgili, E.T.S.E.Q., Depart. d'Enginyeria Química, 43007 Tarragona, Spain

#E-Mail: frederic.leroy@urv.net,

MFI-type zeolites [1] are compounds defined by the chemical formula $Na_xAl_xSi_{96-x}O_{192}$. Sodium cations are free while Aluminium is substituting Silicium of the structure. When the ratio Si/Al>1000, the zeolite is named silicalite, while below, one calls it Na-ZSM5 zeolite. These MFI-type zeolites can be represented by a network of interconnected channels. The distance between two intersections is roughly 1.0nm while the diameters of channels are about 0.55nm. There are two groups of channels: Straight and sinusoidal ones. This channels' diversity leads to a highly anisotropic diffusivity. Zeolites should be considered as open framework materials, and they are gaining increasing importance in industrial applications such as catalysis, but also separation by sieving when the dimensions of the pores are close to those of the molecules. A crucial role is played in these processes by adsorption and transport of the guest molecules.

We present a study of the equilibrium diffusion of a set of *n*-alkanes (methane, *n*-butane, *n*-hexane, *n*-octane and *n*-decane) in MFI-type zeolites at 300K. The work can be divided in two parts:

A Molecular Dynamics (MD) simulation of the self-diffusion coefficients of the *n*-alkanes set in the purely siliceous (ratio Si/Al infinite) silicalite zeolite.

A comparison of MD computations to Quasi-Elastic Neutron Scattering (QENS) experiments.

MD simulations were carried out at different loadings using both flexible and rigid framework models. It is shown that the self-diffusion is enhanced using a flexible lattice for the lowest loadings and the shortest alkanes (methane and *n*-butane), while no effect is observed for the longest. Thanks to the analysis of translational vibrational states density spectra (power spectra) of methane as well as host-guess interaction energy distribution, it is allowed to conclude that the effect of the framework vibrations is to lower slightly the barriers along the diffusive path and to displace minima to higher energies, yielding to a faster diffusion [2].

Two conceptually different models of alkanes are used to carry out calculations in the rigid framework. First, the United Atom (UA) description [3] according to which methylene and methyl groups are each modeled as a single interaction center. Second, the Anisotropic United Atom (AUA) according [4] to which the methylene and methyl

groups are each given a mass center and an interaction center slightly displaced from the mass one so that the existence of Hydrogen atoms should be taken into account. The UA model yields to a comparable self-diffusion coefficient of n-butane and n-decane at infinite dilution. While AUA model yields a constant and deadened decrease of the diffusivity respect to the alkanes' length.

To conclude this part, it should be noticed that whatever the model used, MD in purely siliceous silicalite yields to a self-diffusion coefficient of the same order of magnitude, $10^{-9} m^2 s^{-1}$, from n-butane to n-decane.

QENS experiments in Na-ZSM5 zeolites [5] report a decrease of diffusion with a rough law of proportionality to 10^{-n} where n is the number of Carbon atoms per n-alkane. This trend is different of that observed by MD in purely siliceous silicalite. But, given the set of avalaible datas, a direct comparison was not possible.

Then, as a first approach, MD simulations of n-butane, n-hexane and n-octane at loadings comparable to those of experiments were carried out by modeling the Sodium cations like fixed steric hindrances on the main diffusive path of alkanes. This would correspond to strong interactions between the cations and the structure while the chosen position would be the worst situation a diffusive guest molecule could encounter. It is computed that the effect is to slow down the diffusion.

QENS experiments were carried out to obtain the self-diffusion coefficient of n-octane in silicalite. The measured diffusivity is increased compared to that in Na-ZSM5.

Finally, when moving from silicalite to Sodium containing zeolite, n-alkanes diffusivity observes the same trend of slowing down in MD and QENS, and given the standard error associated to each method, the agreement can be considered as good [6].

References

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