diffusion-fundamentals

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

Diffusion of n-Alkanes in MFI-Type Zeolites: a Comparative Study with Different Measuring Techniques

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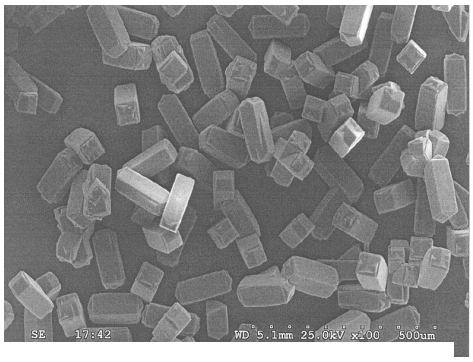
1. Introduction

An international research collaboration has been initiated in order to study in detail diffusion of molecules in zeolitic crystals using a variety of experimental techniques which can be used to probe these systems over different time scales and length scales. The aim is to provide sufficient experimental information that can lead to a better understanding of the main mechanisms that influence mass transfer in nanoporous materials. To guarantee the validity of the results, the studies are all performed on crystals purposely synthesized.

In this contribution we report our results on MFI type zeolites for the homologous series of n-alkanes. The experimental results clearly show an increase in diffusional time constants with the increase of length scale of the observation, which is an indication that in these zeolites the effect of internal inhomogeneities in the crystalline structure has a significant impact on mass transfer.



2. Experimental results and conclusions

The different techniques, quasi-elastic neutron scattering (QENS), pulsed field gradient (PFG) NMR and zero length column (ZLC) measurements, pose some specific requirements on the quantity and size of the zeolite samples needed. In

particular QENS measures diffusional paths over short length scales and requires relatively large sample quantities, 5-10 grams, without a constraint on the actual crystal size. PFG NMR measures diffusional paths over the range of micrometers and requires, as a result, crystals of fairly large size, i.e. of the order of tens of micrometers in the optimum case and still relatively large quantities of some hundred milligrams.

The ZLC measures the mass transfer to the entire crystals and requires large crystals, tens of micrometers, for fast diffusing species but requires only 1-2 mg. ZSM-5 and Silicalite-1 crystals were purposely synthesised and X-ray diffraction patterns of all the samples showed that the specimens were of high quality. All partners have studied the identical specimens. Figure 1 shows the image of the ZSM-5 sample. Figure 2 shows the representative comparison of diffusivities in ZSM-5 and Silicalite-1 as a function of the carbon number at 423 K.

The experimental results indicate a decrease in the diffusivity with the time/length scale of the experiment. The QENS data represent the intrinsic intracrystalline diffusivity, while PFG NMR shows a lower value by up to an order of magnitude which can be seen as an indication of the presence of internal barriers to the movement of the molecules [2]. The ZLC results show a diffusivity which is approximately two orders of magnitude lower than the PFG NMR results and is consistent with the proposed mechanism. To verify the internal nature of the mass transfer resistance the partial loading experiment [3] was performed. In the range of carbon numbers investigated the diffusivities measured by all three techniques were found to be monotonically decreasing.

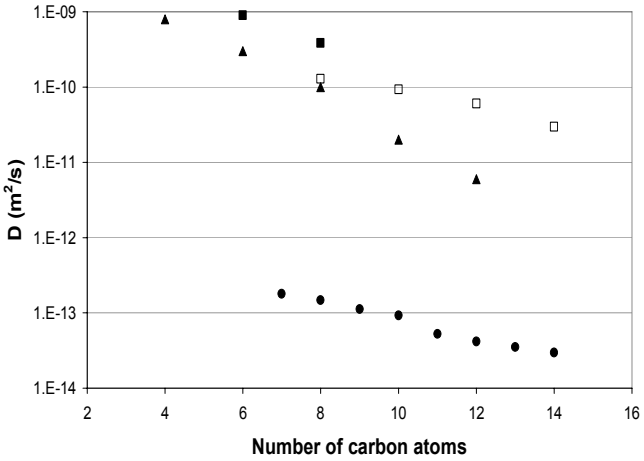


Figure 2. Comparison of experimental results at 423K.
■ QENS new data; □ QENS [1]; ▲ PFG-NMR ; ● ZLC.

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