

ABSTRACT

MASS TRANSPORT OF LARGE MOLECULES IN ZEOLITES

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Mass transport in zeolitic materials has been the object of extensive research in the last several decades. Many ambiguities and unanswered questions still subsist. In order to obtain a more complete understanding of the phenomena involved, we conducted a careful and consistent study of different adsorbate/adsorbent systems.

The work has been approached on three levels, roughly corresponding to three different physical scales.

First, mass transport in a bed of zeolite particles is analyzed. The importance of transport in the bulk-gas phase relative to intra-crystalline diffusion is discussed. A simple heterogeneous transport model is presented in order to illustrate these concerns. The validity of the model was tested in the simulation of a set of ^{129}Xe NMR experiments for the benzene/ZSM-5 system.

In the second part, attention is focused on transport in a single zeolite particle exhibiting a surface resistance. The diffusion of *n*-paraffins in zeolite T is studied. A strategy for separation of the internal and external mass transfer resistance parameters is

developed, based on the temporal moments of the gravimetric sorption data. Both resistances are strongly dependent on zeolite occupancy. The external resistance is the controlling process at low loadings, while at high loadings mass transfer is diffusion-controlled. No evidence was found of the "window effect" reported by Gorring for the intra-crystalline diffusivities in this system.

Finally, intra-crystalline diffusion alone is addressed. A simultaneous thermal analyzer was used to study the diffusion of cyclohexane and several alkyl-cyclohexanes in silicalite. Heats of sorption as well as diffusion coefficients can be estimated from these experiments. Zero length chromatography was also used for some of the adsorbates. The following trend in diffusion rates was observed: *trans*-1,4-dimethylcyclohexane >> methylcyclohexane > cyclohexane > ethylcyclohexane, *cis*-1,4-dimethylcyclohexane. A comprehensive interpretation of the experimental results is presented, using basic qualitative arguments of Transition State Theory. Entropic effects may play a significant role in this system.