

Concentration and temperature dependence of the diffusivity of *n*-hexane in MFI-zeolites

Alina O. Koriabkina^a, Arthur M. de Jong^{b,*}, Emiel J.M. Hensen^a,
Rutger A. van Santen^a

^a Laboratory of Inorganic Chemistry and Catalysis, Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

^b Accelerator Laboratory, Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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Abstract

The concentration dependence of the self-diffusivity of *n*-hexane in large crystals of silicalite-1 and HZSM-5 zeolites has been investigated with positron emission profiling (PEP) in the temperature range of 393–483 K. A monotonic increase in the diffusivity was observed with increasing alkane loading for both zeolites up to 4 molecules per unit cell. The diffusion coefficient in HZSM-5 was approximately half of that in silicalite-1 due to the interaction of *n*-hexane with the Brønsted acid sites. The increase in the diffusivities with the loading is assumed to be caused by the repulsive interactions between the molecules adsorbed in the channel intersections and the adjacent straight channel. The apparent activation energy of diffusion was measured to be independent of the partial pressure of alkane, while the jump frequency increased. In HZSM-5 zeolite the apparent activation energy decreased with the partial pressure due to stronger interactions between *n*-hexane and the acid sites at low pressures.

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1. Introduction

MFI-type zeolites are widely used in the petroleum industry as molecular sieves in separation processes and as catalysts for hydrocarbon conversion processes. Amongst others, hydroisomerization of *n*-hexane is one of the important reactions in the oil refinery to upgrade motor fuels. This explains the large interest in the diffusion and adsorption of hydrocarbons in zeolites over the last few decades. It is a well-known phenomenon that diffusion in zeolites is influenced by the concen-

tration of the adsorbed component [1]. A detailed understanding of this dependence might allow one to enhance or model the separation or catalytic conversion of hydrocarbons.

Five types of concentration dependence of self-diffusion in zeolites (see Fig. 1) have been described in the literature [1]: (1) the diffusivity decreases monotonically with pore occupancy; (2) the diffusivity is constant up to medium pore filling, while a decrease is observed at high loadings; (3) at low concentration the diffusivity monotonically increases and then remains constant with further increase in the loading; (4) the diffusivity has a maximum at certain pore filling; (5) the diffusion coefficient monotonically increases with the concentration. The diffusion behavior is mainly determined by adsorbate–adsorbate and adsorbate–zeolite matrix interactions.

* Corresponding author. Tel.: +31 40 247 4051; fax: +31 40 243 8060.

E-mail address: a.m.de.jong@tue.nl (A.M. de Jong).

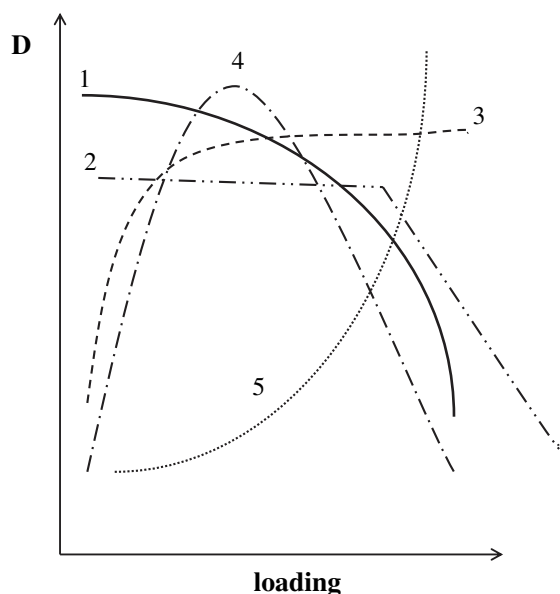


Fig. 1. Schematic drawing of the various types of the concentration dependencies of the diffusivity D in zeolites.

Usually, type-1 concentration dependence is observed for saturated hydrocarbons in silicalite. Frequency response (FR) [2] and square wave [3] methods indeed showed a decrease in the diffusivity for n -hexane in silicalite with loading. The diffusivities of smaller alkanes like methane, ethane and propane in silicalite become also lower with increasing concentration as shown by Caro et al. [4]. A number of theoretical studies have been devoted to this issue [5–8]. Kinetic Monte-Carlo simulations [5] have shown that in MFI-type zeolites, the diffusivity strongly depends on the loading and the zeolite topology. For silicalite, the diffusivity decreases with loading and the dependence can be approximated by a stretched exponential [5]. A similar behavior was found for the diffusion of linear and branched alkanes in various zeolites using molecular dynamics simulations [9].

In silicalite-1, which consists of straight and zigzag channels, the diffusion coefficient obtained from experimental observations or deduced from computer simulations is the average value of the contribution of the diffusivities in both channels, which in their turn depend on the pore occupancy. Recently, theoretical [10] and experimental [11,12] studies indicate different diffusion behavior of hydrocarbon molecules in straight and sinusoidal channels of silicalite-1. Using the FR method that is able to distinguish diffusion in these channels Song and Rees [11] observed an increase in n -hexane diffusivity in straight channels of silicalite with increasing n -hexane loading. On the other hand, an average n -hexane diffusivity determined from NMR experiments [13] under similar conditions decreased with concentration. The details of the diffusion mechanism are still not completely understood.

In HZSM-5 zeolite, the diffusivity is also influenced by the presence of acid sites as well as geometrical peculiarities of the zeolite framework. In the presence of protons, as revealed by Monte-Carlo simulations [14], the diffusivity might exhibit either of the five types of behavior mentioned above. Concentration, location and strength of the acid sites are additional factors that determine this dependence [14].

In this study, the diffusion of n -hexane in silicalite-1 and HZSM-5 has been investigated with the tracer exchange positron emission profiling technique (TEX-PEP) [15]. TEX-PEP is an in situ technique based on the application of radio-labelled molecules to the investigation of diffusion and adsorption processes of the molecule of the interest in various materials, in this case, alkanes in zeolites. The advantage of TEX-PEP compared to other techniques is that it allows to measure the self-diffusion coefficient and moreover, the adsorbed concentration of the component simultaneously. Experiments are performed in the absence of concentration gradients. In essence, the diffusivity is measured by following the concentration of the radio-labelled hexane molecules upon a step in its concentration in an (large) excess flow of unlabelled hexane. In this way, the total hydrocarbon concentration is not perturbed and chemically speaking, the system remains under steady-state conditions. Hence, the measured diffusivities are self-diffusion coefficients. The use of non-pelletized large zeolite crystals allows to provide micropore diffusion limitation conditions and to simplify the interpretation of the experimental data. The influence of the concentration on the self-diffusion and the activation energy of diffusion have been investigated for silicalite-1 and HZSM-5 zeolites.

2. Experimental section

The PEP technique is a non-invasive in situ radio-chemical method using β^+ -emitting isotopes [16]. The method is based on monitoring the tracer molecules *inside* the zeolite packed bed. In order to investigate diffusion and adsorption of alkanes in zeolites, ^{11}C -labelled hydrocarbons are used. The ^{11}C isotope is produced via irradiation of a nitrogen target with 12 MeV protons from the 30 MeV AVF Cyclotron of the Eindhoven University of Technology.

The radio-labelled hydrocarbons (C_1 – C_6 alkanes) are produced from ^{11}CO and non-labelled 1-pentene using a homologation reaction. Detailed information about this process is available [17]. In order to be used in the tracer-exchange experiments, the hydrocarbon of interest (n -hexane) is separated from the reaction products using a chromatographic column.

During the tracer-exchange experiments, a constant flow of non-labelled hydrocarbon (n -hexane) in a carrier

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