Study of molecular mobility of fluid in zeolite NaX

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Abstract

The self-diffusion of n-decane in zeolite NaX was studied by NMR PFG method. The situation when the liquid was only in the crystalline channels was studied in details. The restricted molecular motion of liquid in the crystalline channels was observed. The reasons of the anomalous self-diffusion of n-decane in zeolite bed were stated. The technique of the determination of the genuine self-diffusion coefficient in such porous systems was proposed. The genuine self-diffusion coefficients for system NaX/n-decane were obtained. © 2001 Elsevier Science Inc. All rights reserved.

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1. Introduction

The research of molecular mobility of fluid in such porous medium as zeolite is constantly of great scientific interest in connection with a capability of its application as highly effective heterogeneous catalysts, molecular sieves and adsorbents. At the present time a number of works, devoted to the study of the fluid self-diffusion in zeolite bed by NMR methods have been made. The study of the diffusion behavior of fluid inside the channels of zeolite crystal is of great interest for the researchists. As the channel diameters and diameters of fluid molecules, as a rule, are commensurable, in a number of cases it results to the unusual self-diffusion.

2. Materials and method

The measurements were done by NMR method with PFG. It has been carried out with the homebuilt NMR spectrometer at a proton resonance frequency of 60 MHz. The maximum magnitude of the pulse gradient (g) was 100 T/m. The usual three-pulse sequence of stimulating spin-echo was mainly applied. In the experiment stimulated spin echo decays or diffusion attenuation ($A(k)$), where $k^2 = \gamma^2\delta^2 g^2$ (γ - gyromagnetic ratio of a proton, δ - duration of pulsed gradient) were registered. The diffusion attenuation

was recorded in the conditions of scanning of the magnitude of g at the fixed parameters of δ and t. Decane was introduced into zeolite NaX. Crystalline of the NaX has a system of the three-dimensional intersected channels, all the channels are equivalent and free diameters are identical for all the channels. The size of the diameter is 0,74 nm [1]. The crystalline forms the spherical particles the diameter of which is above $1–1.5\,\mu$m. The measurements were made in the temperature range 303–363 K. The times were varied in the interval 2–450 ms. The maximum filling of the intracrystalline channel by n-decane was 0.10 mass content.

3. Results and discussion

On Fig. 1 the time dependencies of $A(k)$ obtained for the sample with the contents of n-decane 0.08 are presented. As it can be seen from the plots, the form of the $A(k)$ is complex and it depends on the t. The reasons causing the non-exponential of $A(k)$, can be stipulated by a lot of factors therefore we shall consider the behavior of the mean self-diffusion coefficient ($\bar{D}$), which was extracted from the initial slope of $A(k)$.

The time dependency of the $\bar{D}$ for the sample with the concentration of fluid 0.08 is represented on Fig. 2 for temperatures: 303 and 363 K. As it is shown on the plot, the experimental dependencies of $\bar{D}$ in a large range of the t can be satisfactorily explained by the dependency of the type $\bar{D} \sim t^n$ where $n = 0,5 \div 0,6$. It is known [2–3], that for the single-file diffusion regime the behavior of the self-diffu-

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