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Adsorption and diffusion of light alkanes on nanoporous faujasite catalysts investigated by molecular dynamics simulations

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Abstract

Molecular dynamics simulations were performed for ethane, propane, and *n*-butane in siliceous faujasite for different numbers of molecules per unit cell (loadings) at 300 K. Both the adsorbed molecules and the zeolite framework were modeled as flexible entities. A new semiempirical analytical potential function for the systems was constructed. From the mean-square displacement of the molecules, self-diffusion coefficients of 18.7×10^{-5}, 13.3×10^{-5}, and 4.3×10^{-5} cm^2/s were calculated for ethane, propane, and *n*-butane, respectively at a loading of 8 molecules/unit cell. They compare well with experimental values from pulsed-field gradient NMR measurements (10×10^{-5}, 9×10^{-5}, and 6×10^{-5} cm^2/s, respectively). Besides depending on the size of the hydrocarbon, the heats of adsorption and self-diffusion coefficients also strongly depend on the loading of adsorbate molecules. The results suggest that the new intermolecular force field can reasonably describe the adsorption and diffusion behavior of ethane, propane, and *n*-butane in faujasite zeolite.

Keywords: Molecular dynamics; FAU; Ethane; Propane; *n*-butane; Adsorption; Diffusion

1. Introduction

Zeolites are microporous materials with regular crystalline structures. They are widely employed as molecular sieves in various industrial processes, such as adsorption, catalysis, purification, and separation of mixtures [1–3]. One of the industrially most important zeolites is faujasite. Faujasite is a 3-dimensional zeolite with cubic symmetry and has a 12 membered ring pore opening with a diameter of 7.4 Å that provides access to a supercage with a diameter of 12.4 Å. Each unit cell of faujasite is composed of eight supercages.

The adsorption and diffusion of light alkanes in zeolites have been widely studied because of its theoretical and technological importance and numerous investigations have been reported using both experimental [4–6] and theoretical [7–11] techniques. Especially the influence of the molecular geometry, the Si/Al ratio, the Brønsted acid site, and the effect of adsorbate-zeolite interactions on the adsorption and diffusion of adsorbates within zeolites have been widely studied [1,2,12].

A good knowledge of the adsorption and diffusion behaviors of the guest molecules in zeolitic hosts is prerequisite before the mechanisms of processes in petrochemical applications can be rationally controlled. However, the adsorption and diffusion of guest molecules in zeolitic hosts are complicated and therefore it is, in general, very difficult to interpret microscopic and dynamical diffusion processes by experimental data only. Computer

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simulations, such as molecular dynamics (MD) can provide a powerful complimentary approach to study the adsorption and diffusion properties of a variety of guest molecules in zeolites [13]. Several studies have applied this method to obtain new insights into the adsorption and diffusion mechanism of alkanes in zeolites [7,14–21]. Nowak et al. [22] used MD simulations to compute diffusion characteristics of methane, ethane, and propane in silicalite. For small adsorbates, such as methane and ethane, good agreement with experimental data was found, but not for propane. The rigid framework/molecule approximation applied in this study should have no dramatic effect [23] and therefore a mass effect might be responsible for the discrepancy. Titiloye et al. [24] used molecular mechanics (MM) to investigate the adsorption of linear hydrocarbons in silicalite, H-ZSM-5, and faujasite found that the relaxation of both framework and adsorbed molecules influences the calculated heat of adsorption.

In the present study, we explore the ability of full atomistic molecular dynamics (MD) simulations to predict the adsorption and diffusion of ethane, propane, and *n*-butane in siliceous faujasite as a function of its loading. We chose to model the siliceous analogue of faujasite as this allows us to separate the effect of the framework geometry on the adsorption from the effect of aluminum and the counterions. In contrast to most former studies, the zeolite framework and adsorbate molecules are modeled as flexible entities. The computed results are compared with experimental data.

2. Methodology

2.1. Construction of the siliceous faujasite zeolite

The faujasite unit cell is cubic with cell dimensions of $a = b = c = 24.20$ Å and contains 192 silicon and 384 oxygen atoms (SiO_2). The atomic coordinates for the faujasite lattice are taken from X-ray diffraction measurements reported by Olson and Dempsey [25] (Fig. 1).

2.2. Potential parameters

2.2.1. Intramolecular potential parameters for faujasite

The interaction model for the lattice is a generalized valence force field (GVFF), taken from the work of Nicholas et al. [26]. In this approximation, the potential energy of the framework system is presented as a function of Si–O bond stretchings, O–Si–O and Si–O–Si angle bends, and of bond torsions. The bond stretches and O–Si–O angle bends are approximated as simple harmonic potentials. The Si–O–Si–O dihedral contributions were modeled with a cosine potential. The mathematical expressions of all terms are given in Table 1. The values of the various force constants and equilibrium values were derived from the experimental data and are shown in Table 2.

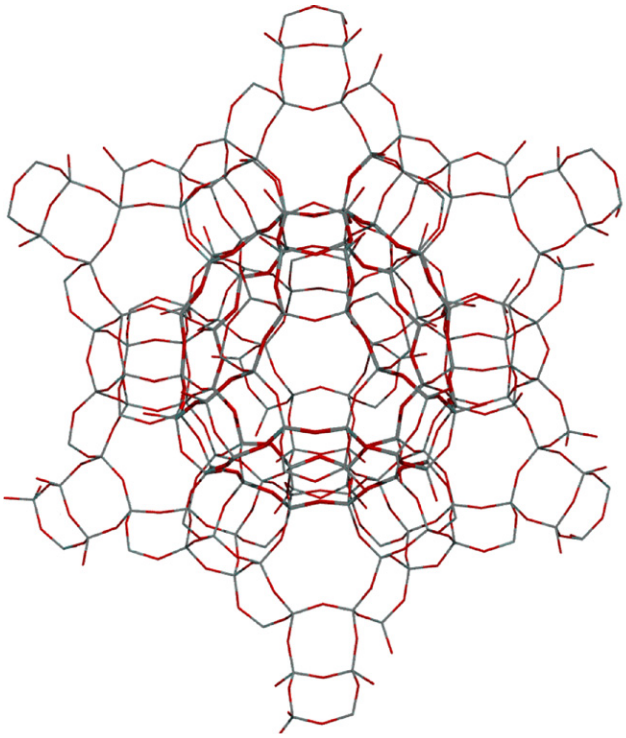

Fig. 1. Faujasite zeolite structure showing the large cavity.

Table 1
Terms in the analytical intramolecular potential for siliceous faujasite zeolite

Type of term	Expression
Bond	$U(r_{ij}) = \frac{k}{2}(r_{ij} - r_0)^2$
Angle	$U(\theta_{jik}) = \frac{k}{2}(\theta_{jik} - \theta_0)^2$
Dihedral angle	$U(\text{Ø}) = A[1 + \cos(m\text{Ø} - \delta)]$
Lennard-Jones	$U(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$
Coulomb	$U_{\text{coul}} = \frac{q_i q_j}{r_{ij}} f \quad f = 332.13$

2.2.2. Potential parameters for the alkanes and alkane-faujasite

The intramolecular valence force field parameters for the alkanes were taken from the works of Nicholas et al. [7], Dumont and Bougeard [8], and Henson et al. [9]. The intermolecular guest–guest interactions as well as the interactions between guest molecules and siliceous faujasite were expressed as the sum of Lennard-Jones (LJ 12-6) and Coulomb terms (Eq. (1)):

$$U(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{r_{ij}} \tag{1}$$

where r is the distance between one atom of zeolite and one of the adsorbate molecule. The numerical values of the LJ-parameters for the C–Si, C–O, H–Si, and H–O interactions were obtained in the following way: At first the Lorentz–Berthelot combination rules (Eq. (2)) were used to calculate